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amine, $(C_6H_4{:}C_2O_2{:}N{\cdot}CH_2)_3N,CH_3{\cdot}CO_2H$, separated with a molecule of acetic acid in colourless prisms, m. p. 222—223° (22 g.) (Found: C, 62·8; H, 3·8. $C_{29}H_{22}O_8N_4$ requires C, 62·8; H, 4·0%). Recrystallisation from pyridine gave the free *triphthalimidotrimethylamine* in colourless prisms, m. p. 235° (Found: C, 65·8; H, 3·5; N, 11·2. $C_{27}H_{18}O_6N_4$ requires C, 65·6; H, 3·6; N, 11·3%). The molecule of acetic acid, which is slowly lost when the compound is heated in a vacuum at 100°, may be present as acetic acid of crystallisation, or may be united to the tertiary amine group to form an unstable acetate. The formation of an acetate is most improbable, however, in view of the very feebly basic properties of the tertiary amine group in triaminotriethylamine (Mann and Pope, *loc. cit.*).

When triphthalimidotrimethylamine (10 g.) was heated gently under reflux with hydrochloric acid (1 : 1 by vol.; 300 c.c.), a complete solution was obtained after about 8 hours. This solution contained, however, only phthalic acid, formaldehyde, and ammonium chloride. Ing and Manske (J., 1926, 2348) have recently described a far less drastic method of hydrolysing phthalimido-compounds by treating them in alcoholic suspension with hydrazine hydrate. A suspension of triphthalimidotrimethylamine (3 g.) in alcohol (100 c.c.) was therefore heated on the water-bath with hydrazine hydrate (5 c.c. of 50% aqueous solution). The clear solution, which was rapidly obtained, soon deposited a white, gelatinous precipitate, which, after heating for 2 hours, was filtered off, washed, and recrystallised from alcohol. This compound, which did not melt below 330°, was probably *triphthalylhydrazidotriamino-trimethylamine*, $N\left(CH_2{\cdot}NH{\cdot}C\begin{matrix}C_6H_4\\N{\cdot}NH\end{matrix}>CO\right)_3$, but was too unstable to be obtained pure (Found, after consecutive alcoholic recrystallisations: N, 25·5, 26·7. $C_{27}H_{24}O_3N_{10}$ requires N, 26·2%). When this product was treated with cold dilute hydrochloric acid, a thick suspension of phthalylhydrazide, $C_6H_4{:}C_2O_2{:}(NH)_2$ (Found: N, 17·4. Calc. for $C_8H_6O_2N_2$: 17·3%), separated with evolution of heat, whilst the solution contained formaldehyde and ammonium chloride.

It is clear from these results that $\alpha\alpha'\alpha''$-triaminotrimethylamine cannot be isolated owing to its ready hydrolysis to formaldehyde and ammonia, but is stable in the form of its triacyl derivatives. Its behaviour is thus closely akin to that of the parent methylenediamine, $CH_2(NH_2)_2$, which also hydrolyses readily into formaldehyde and ammonia, but gives stable diacetyl and dibenzoyl derivatives (Pulvermacher, *Ber.*, 1892, **25**, 310; Einhorn and Mauermayer, *Annalen*, 1905, **343**, 307) and also a stable diurethane,

$$CH_2(NH{\cdot}CO_2Et)_2$$

(Curtis, *J. pr. Chem.*, 1895, **52**, 225; Conrad and Hock, *Ber.*, 1903, **36**, 2206).

Phthalbromomethylimide unites vigorously with pyridine to give *phthalimidomethylpyridinium bromide*, $C_6H_4{:}C_2O_2{:}N{\cdot}CH_2{\cdot}NC_5H_5Br$, which, after recrystallisation from alcohol, is obtained in large, colourless prisms, m. p. (on rapid heating) 244° (Found : Br, 25·2. $C_{14}H_{11}O_2N_2Br$ requires Br, 25·1%). This quaternary ammonium bromide, when boiled with dilute hydrochloric acid (1 : 1 by vol.), gave pyridine, ammonia, phthalic acid, and formaldehyde.

Phthalbromomethylimide reacts violently with anhydrous diethylamine, and, even when the reaction occurs in dilute xylene solution, phthalimide is the chief product. Pucher and Johnson (*loc. cit.*) have shown that phthalimide is also produced by the action of potassium cyanide, ethyl sodioacetoacetate, or ethyl sodio-γ-diethoxyacetoacetate on phthalbromomethylimide, and the latter, they suggest, often acts as if it were a methyleneammonium bromide of constitution $C_6H_4{:}C_2O_2{:}N(Br){:}CH_2$. Its reactions with ammonia and pyridine described above are, however, those of the true phthalbromomethylimide, $C_6H_4{:}C_2O_2{:}N{\cdot}CH_2Br$.—University Chemical Laboratory, Cambridge. [*Received, November 25th*, 1926.]

The Action of Nitrous Acid on ar-*Tetrahydro-α-naphthol and on* 5 : 8- *and* 5 : 6(*or* 7 : 8)-*Dihydro-α-naphthols.* By Frederick Maurice Rowe and Esther Levin.

Schroeter's statement (*Annalen*, 1922, **426**, 104, 152) that nitrous acid converts *ar*-tetrahydro-α-naphthol into 4-nitroso-*ar*-tetrahydro-α-naphthol, greenish-yellow needles, m. p. 161—163° (decomp.), led the authors to re-examine the product of this reaction, yellow needles, m. p. 163° (decomp.), obtained by Green and Rowe (J., 1918, **113**, 965) and described as 4-nitro-*ar*-tetrahydro-α-naphthol. That this product was really the 4-nitroso-compound has now been proved as follows : An aqueous suspension of *ar*-tetrahydro-α-naphthaquinone was mixed with an aqueous solution of hydroxylamine hydrochloride, the mixture was kept for 24 hours and then rendered alkaline and filtered, and the filtrate was acidified. The precipitated *ar*-tetrahydro-α-naphthaquinoneoxime (4-nitroso-*ar*-tetrahydro-α-naphthol) crystallised from dilute alcohol in yellow needles, m. p. 163° (decomp.) (Found : * C, 68·1; H, 6·3; N, 7·8. Calc. : C, 67·8; H, 6·2; N, 7·9%) and was identical in all respects with Green and Rowe's "4-nitro"-compound. Further, the finely powdered compound, prepared in either way, was oxidised

* To obtain accurate results, it was essential to carry out the combustions extremely slowly.

to the corresponding nitro-derivative by adding 2 g. in small portions at a time to a mixture of 3 c.c. of nitric acid (*d* 1·4) and 9 c.c. of water at 40°. 4-*Nitro*-ar-*tetrahydro*-α-*naphthol* crystallises from toluene in faintly coloured needles, m. p. 123°; it is not volatile with steam and forms yellowish-brown salts (Found: C, 62·2; H, 5·9; N, 7·3. $C_{10}H_{11}O_3N$ requires C, 62·2; H, 5·7; N, 7·2%).

Finally, the products of the interaction of an aqueous solution of phenylhydrazine hydrochloride and a glacial acetic acid suspension of *ar*-tetrahydro-α-naphthaquinone, and of a mixture of 4-nitroso-*ar*-tetrahydro-α-naphthol and aniline acetate at the temperature of a boiling water-bath, were identical with benzeneazo-*ar*-tetrahydro-α-naphthol, prepared by coupling benzenediazonium chloride with *ar*-tetrahydro-α-naphthol (Jacobson and Turnbull, *Ber.*, 1898, **31**, 898).

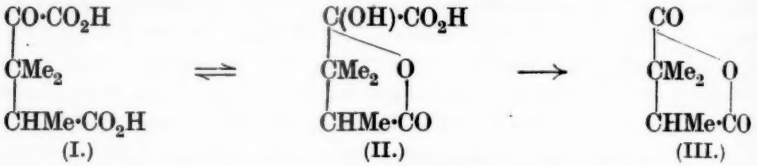
Also the compounds described as 4-nitro-5 : 8-dihydro-α-naphthol and 4-nitro-5 : 6(or 7 : 8)-dihydro-α-naphthol (J., 1921, **119**, 2024) gave, on very slow combustion, results which show that they are really the 4-nitroso-compounds: 4-*Nitroso*-5 : 8-*dihydro*-α-*naphthol*, brownish-yellow needles, m. p. 161° (decomp.) (Found: C, 68·6; H, 5·2; N, 7·9. $C_{10}H_9O_2N$ requires C, 68·6; H, 5·1; N, 8·0%); 4-*nitroso*-5 : 6(or 7 : 8)-*dihydro*-α-*naphthol*, yellow needles, m. p. 162° (decomp.) (Found: C, 68·7; H, 5·3; N, 7·8. $C_{10}H_9O_2N$ requires C, 68·6; H, 5·1; N, 8·0%). These compounds are too sensitive to oxidation to permit their conversion into the corresponding nitro-derivatives with nitric acid; moreover, the dihydro-α-naphthylamines cannot be oxidised to dihydro-α-naphthaquinones (J., 1922, **121**, 1001).—The University, Leeds. [*Received, December 8th*, 1926.]

LXXVIII.—*Ring-chain Tautomerism. Part XV. The Hydroxy-lactone Type.*

By Eugene Rothstein and Charles William Shoppee.

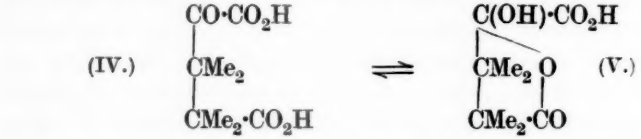
In Part I of this series (Kon, Stevenson, and Thorpe, J., 1922, **121**, 654; see also Rothstein, Stevenson, and Thorpe, J., 1925, **127**, 1073), it was shown that the acid $C_8H_{12}O_5$ (Balbiano's acid) is a mixture of two tautomeric individuals (I and II). The evidence for the presence of the tautomeride (II) consisted in the fact that on treatment with *o*-phenylenediamine in acetic acid solution an acidic addition product, which was not a salt, was formed, and on heating this, or on boiling the two substances together, the usual quinoxaline derivative was formed. There was additional evidence for the existence of the hydroxy-lactone isomeride (II), inasmuch

as the latter gave off carbon monoxide, with the formation of trimethylsuccinic anhydride (III), when heated above its melting point (*loc. cit.*).



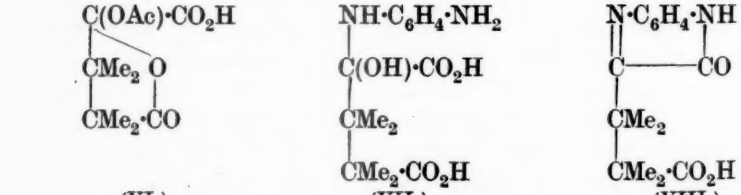
(I.) (II.) (III.)

The authors have now investigated the methyl derivative (IV) of Balbiano's acid (Francis and Willsdon, J., 1913, **103**, 2238), because it seemed to them that the presence of the second *gem*-dimethyl group should stabilise the hydroxy-lactonic form (V) of the acid. This has been found to be the case.



When the acid (V) was titrated with baryta solution, it behaved as a monobasic acid. When it was boiled with *N*/100-baryta, the hydroxy-lactone ring underwent fission to the extent of about 40%. Similar treatment with *N*/10-baryta increased the fission to 95%, but complete fission could not be obtained. Balbiano's acid, under similar conditions, always yielded the normal barium salt (of the dibasic acid). The above figures were also obtained after the acid (V) had been esterified to the dimethyl ester and then regenerated by hydrolysis.

Another striking difference between the acid (V) and Balbiano's acid, indicating the difference in stability of the respective hydroxy-lactonic rings, is that the former yielded an *acetyl* derivative (VI) on treatment with acetic anhydride. This derivative decomposes sodium hydrogen carbonate and behaves as a monobasic acid on titration.



(VI.) (VII.) (VIII.)

Like Balbiano's acid, the compound (V) gives an *addition product* (VII) with *o*-phenylenediamine, and also the *condensation product*

(VIII). There is, however, an important distinction between the two compounds. Whereas the condensation product can be obtained from Balbiano's acid by boiling the acid itself with *o*-phenylenediamine, the only methods by which the corresponding derivative is formed from the tetramethyl acid are by heating the addition product, by fusing the acid and the phenylenediamine together, and by fusing the dimethyl ester with the same compound.

It is evident, therefore, that the hydroxy-lactone phase is the stable form of the tetramethyl compound, and, unlike Balbiano's acid, in solution this is not a tautomeric mixture of (IV) and (V). The presence of alkalis or acids, however, tends to shift the equilibrium in favour of the ketonic form.

It is therefore now possible to record the existence of three members of an homologous series, differing from one another in the possession of an additional methyl group, in which the influence of this group on the carbon tetrahedral angle is clearly demonstrated by the chemical and physical properties of the substances described. The ββ-dimethyl compound is static as a hydrated ketone, the ββγ-trimethyl acid (I and II) is a tautomeric mixture of the ketonic and the hydroxy-lactonic form, whilst, finally, the ββγγ-tetramethyl acid (V) is static as the hydroxy-lactone.

Experimental.

Hydroxy-lactone of α-Keto-ββγγ-tetramethylglutaric acid (V).—The acid was prepared from bromohydroxyphorone by the method of Francis and Willsdon (*loc. cit.*). After recrystallisation from toluene, or ethyl acetate and light petroleum, it melted at 140° (Found: C, 53·2; H, 6·9. Calc.: C, 53·4; H, 6·9%).

Titration with *N*/100-baryta solution gave *M*, 202, 204 [Calc.: *M* (monobasic), 202]. When the acid was boiled with *N*/100- and with *N*/10-baryta solution, and then titrated with *N*/20-hydrochloric acid, the values of *M* were 162 and 107, respectively. Balbiano's acid, both on direct and on back titration, gave the value *M*, 95 [Calc.: *M* (dibasic), 94].

When the acid was heated above its melting point, it yielded carbon monoxide (11·9 litres per g.-mol.), and tetramethylsuccinic anhydride was found in the residue.

The dimethyl ester, b. p. 170°/15 mm., was prepared by the action of methyl iodide on the disilver salt, or by Phelp and Tillotson's alcohol-vapour method. It crystallised from benzene, or from chloroform and ligroin, in plates, m. p. 103°. The ester could not be characterised by the formation of ketonic derivatives.

Acetyl Derivative of the Acid $C_9H_{14}O_5$ (VI).—The acid (V) was heated under reflux with acetic anhydride for one hour, and the

excess of the latter was then removed in a vacuum desiccator containing potash. The product, twice crystallised from benzene and petroleum, formed stellate clusters of needles, m. p. 149° (Found : C, 54·0; H, 6·5; *M*, 241. $C_{11}H_{16}O_6$ requires C, 54·1; H, 6·6%; *M*, monobasic, 244).

Addition Product with o-*Phenylenediamine* (VII).—The acid (V) (0·5 g.), dissolved in the minimum of water, was treated with 10% excess of *o*-phenylenediamine, dissolved in glacial acetic acid. On warming and rubbing, a pale buff precipitate appeared, which separated from alcohol in plates, m. p. 160° (Found : C, 58·7; H, 7·1; N, 8·8. $C_{15}H_{22}O_5N_2$ requires C, 58·4; H, 7·1; N, 9·0%).

The substance decomposes sodium hydrogen carbonate, but not sodium hydroxide solution. When heated above its melting point, it loses water and yields the condensation product (VIII).

Condensation Product with o-*Phenylenediamine* (VIII).—(*a*) The acid (V) (0·5 g.) and *o*-phenylenediamine (0·3 g.) were fused together at 165° for ½ hour. After cooling, the product was treated with a small quantity of boiling alcohol; the almost colourless residue crystallised from acetic acid in tiny cubes, m. p. 238—239°. The alcoholic filtrate slowly deposited the addition compound as a buff precipitate.

(*b*) The dimethyl ester (0·4 g.) and *o*-phenylenediamine, similarly heated together, gave the same product.

The substance, after being crystallised twice from acetic acid, melted at 240° (Found : C, 64·9; H, 6·4. $C_{15}H_{18}O_3N_2$ requires C, 65·6; H, 6·6%). It was reprecipitated unchanged from sodium hydroxide solution by hydrochloric acid, and did not decompose sodium hydrogen carbonate. Like the corresponding condensation product of Balbiano's acid, it turned blue litmus violet-red.

One of us (C. W. S.) desires to thank the Commissioners of the 1851 Exhibition for a Senior Studentship, and the Royal Society for a grant towards the expenses of this investigation.

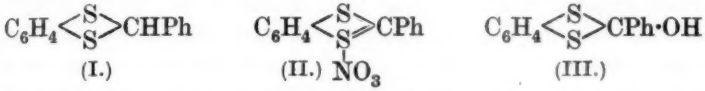
THE UNIVERSITY, LEEDS. [*Received, January 20th*, 1927.]

LXXIX.—*Derivatives of* 2-*Phenyl*-1 : 3-*benzdithiole.*

By WILLIAM ROBERT HARDY HURTLEY and SAMUEL SMILES.

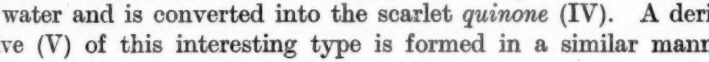
IN a previous communication (J., 1926, 1822), it was shown that 2-phenyl-1 : 3-benzdithiole (I) may be oxidised by nitric acid to the sulphonium nitrate (II), from which the pseudo-base (III) is liberated by alkali. Further experiments on the formation of these sulphonium nitrates have now been made, chiefly with the object of deter-

mining whether the process may be generally applied to other members of this group and whether it is subject to the influence of substituents in the 2-phenyl nucleus. The results are summarised as follows.



(I.) (II.) (III.)

The presence of a nitro-group in the 2-phenyl nucleus is unfavourable to the formation of the sulphonium salt by oxidation; *e.g.*, the *o*-nitrophenyl derivative (type I) is not attacked by the usual agents. On the other hand, methoxy- and hydroxy-groups facilitate the process. The *nitrate* of the 2-*p*-methoxyphenyl derivative (type II) is very easily formed from the mercaptol (type I), whilst the corresponding *pseudo-base* (type III), which has been characterised as the *oxide* (compare *loc. cit.*, p. 1827), yields more stable salts than the unsubstituted derivative. Oxidation of the *p*- and *o*-hydroxy-derivatives proceeds so easily that unless precautions are adopted it ensues during the formation of the mercaptol (type I) from the hydroxy-aldehyde and *o*-dithiolbenzene. Attempts to obtain the pseudo-base from the salts of 2-*p*-hydroxyphenyl-benzdithiole sulphonium (type II) were unsuccessful, since this substance (type III) at the moment of liberation loses the elements of water and is converted into the scarlet *quinone* (IV). A derivative (V) of this interesting type is formed in a similar manner



(IV.) (V.)

from 2′-hydroxy-2-naphthyl-1 : 3-benzdithiole. Oxidation of this naphthyl derivative takes place so readily that it has not been possible to isolate the mercaptol (type I), the product from *o*-dithiolbenzene and 2-naphtholaldehyde in presence of hydrogen chloride being the chloride of the pseudo-base, which with alkaline media yields the unimolecular *quinone* (V). These quinonoid derivatives yield hydrochlorides which at present are assumed to be of the sulphonium type (II).

Experimental.

2-*o*-Nitrophenyl-1 : 3-benzdithiole was obtained by saturating a cooled solution of the dithiol (0·5 g.) and *o*-nitrobenzaldehyde (0·6 g.) in alcohol (15 c.c.) with hydrogen chloride in presence of zinc chloride. The substance (m. p. 106°. Compare Guha and Chakladar, *J. Indian Chem. Soc.*, 1925, **2**, 3) was not attacked by cold nitric acid (*d* 1·4) but was destroyed by the boiling reagent. It gave a yellow bromine derivative.

2-p-*Methoxyphenyl*-1 : 3-*benzdithiole* was obtained in almost theoretical yield by treating a solution of the dithiol (1 g.) and anisaldehyde (1 g.) in alcohol (10 c.c.) at 0° with hydrogen chloride for 15 minutes. The liquid product was kept until it had solidified, and after purification from alcohol it melted at 72° (Found: C, 64·6; H, 4·9. $C_{14}H_{12}OS_2$ requires C, 64·6; H, 4·6%). When a warm (not above 40°) solution of this substance in nitric acid (*d* 1·4) was cooled, the *nitrate* of the base (type II) separated in red needles (Found: HNO_3, 32·9. $C_{14}H_{11}OS_2{\cdot}NO_3,2HNO_3$ requires HNO_3, 32·6%). The base (type III) was liberated from this salt by ice-cold 2*N*-aqueous sodium hydroxide and after being dried it was purified from benzene–light petroleum, 2-p-*methoxyphenyl*-1 : 3-*benzdithiole* 2-*oxide* being obtained in colourless prisms, m. p. 158° (Found: C, 62·7; H, 4·5; *M*, 530. $C_{28}H_{22}O_3S_4$ requires C, 62·9; H, 4·1%; *M*, 538). When an acetone solution of this oxide was mixed with concentrated hydrochloric acid, the *chloride* separated in yellow needles [Found: HCl, 18·7. $(C_{14}H_{11}OClS_2)_3,2HCl$ requires HCl, 19·1%].

2-p-*Hydroxyphenyl*-1 : 3-*benzdithiole* (type I) was prepared as in the case of the *p*-methoxy-derivative, but being more soluble, it was isolated by the addition of ice to the reaction mixture. The purification of the product required care owing to the ease with which it is oxidised. The substance was obtained in needles, m. p. 118°, which persistently retained a faint pink tinge (Found: C, 63·3; H, 4·4. $C_{13}H_{10}OS_2$ requires C, 63·4; H, 4·1%). Oxidation of the mercaptol was conducted by trituration with cooled nitric acid; the *nitrate* was then obtained in orange needles [Found: HNO_3, 11·7. $(C_{13}H_9OS_2)_2,HNO_3$ requires HNO_3, 11·4%].

1 : 3-*Benzdithiole*-2-p-*benzoquinone* (IV) was obtained by treating the foregoing nitrate with aqueous potassium carbonate. It was sparingly soluble in warm benzene, from which it separated in scarlet leaflets, m. p. 212—213° (Found: C, 63·9; H, 3·5. $C_{13}H_8OS_2$ requires C, 63·9; H, 3·5%). The substance was easily reduced by a solution of sulphur dioxide in alcohol and yielded a colourless additive product when treated with aqueous sodium bisulphite. The orange *hydrochloride* was obtained from an acetone solution of this substance (Found: HCl, 13·2. $C_{13}H_9OClS_2$ requires HCl, 13·0%).

1 : 3-*Benzdithiole*-2-β-*naphthaquinone* (V).—The normal mercaptol (type I) could not be obtained by interaction of the dithiol and 2-naphthol-1-aldehyde; instead, the oxidation product was isolated as the hydrochloride (II). A cooled solution of the dithiol (2 g.) and the aldehyde (2 g.) in ether (40 c.c.) was treated with hydrogen chloride and kept for 12 hours. On treatment with aqueous

sodium hydroxide the brown impure salt yielded the desired material (2·4 g.). This separated from acetone in small, red needles, m. p. 165° (Found: C, 69·1; H, 3·5; *M*, 293. $C_{17}H_{10}OS_2$ requires C, 69·4; H, 3·4%; *M*, 294). The substance yielded a colourless additive product with sodium bisulphite, but it was not reduced by an alcoholic solution of sulphur dioxide. The *chloride* was obtained in the usual manner and formed red needles (Found: HCl, 11·2. $C_{17}H_{11}OClS_2$ requires HCl, 11·1%).

2-Styryl-1 : 3-*benzdithiole*, obtained from cinnamaldehyde and the dithiol in the usual manner, formed needles, m. p. 80° (Found: C, 70·2; H, 5·1. $C_{15}H_{12}S_2$ requires C, 70·3; H, 4·7%). When this mercaptol was treated with concentrated nitric acid at 0° for 15 minutes, the *nitrate* of the base (type II) was obtained in orange needles of complex composition [Found: HNO_3, 25·0. $(C_{15}H_{11}S_2 \cdot NO_3)_4, HNO_3$ requires HNO_3, 24·8%]. The base liberated from this nitrate by alkaline media was too unstable for isolation in the pure condition.

In conclusion, we desire to thank the Department of Scientific and Industrial Research for a grant which enabled one of us to take part in these experiments.

KING'S COLLEGE, LONDON. [*Received, January 26th*, 1927.]

LXXX.—*The Optical Resolution of Chloroiodoacetic Acid.*

By ANN MORTIMER MCMATH and JOHN READ.

As a result of a study of certain simple compounds with asymmetric molecules containing one and two carbon atoms, we recently came to the conclusion that the optical stability of such molecules was increased in the series under consideration by the substitution of (*a*) SO_3H for CO_2H, and (*b*) I for Br (J., 1926, 2185). We were thus led to anticipate that chloroiodoacetic acid and bromoiodoacetic acid would exhibit a tendency towards racemisation greater than that of chloroiodomethanesulphonic acid, and possibly of the same general order as that shown by chlorosulphoacetic acid. This anticipation has now been substantiated by the preparation and examination of the two optically active modifications of chloroiodoacetic acid, and it is hoped ultimately to secure corresponding evidence for bromoiodoacetic acid.

Chloroiodoacetic acid, which has been rendered readily available through the introduction of the valuable method of Crompton

and Carter (J., 1923, **123**, 576), may be resolved with ease into its optically active components, either by fractional crystallisation of the hydroxyhydrindamine salts or by fractional precipitation from aqueous solution with brucine.* With both of these bases the less soluble salt is of the type *l*B*l*A, and in practice the use of *d*-hydroxyhydrindamine would be necessary in preparing the optically pure *d*-acid in quantity through the intermediary of this base. Exceptionally, it has proved possible with the aid of brucine alone to prepare, not only the pure *l*-acid, but also the *d*-acid of practically the same rotatory power, by fractional precipitation from aqueous solutions of different concentrations. The highest optical rotatory powers observed in dilute aqueous solution for ammonium *l*- and *d*-chloroiodoacetate are $[M]_D$ — 60° and + 56°, respectively.

The optical stability of ammonium *d*- and *l*-chloroiodoacetate in aqueous solution appears to be somewhat more pronounced than that of the corresponding derivatives of chlorosulphoacetic acid; a further indication is thus afforded of the stabilising influence of the iodine atom, to which we have drawn attention in preceding communications. The decline in optical rotatory power upon heating such solutions is distinct but not rapid; it is accelerated considerably by the addition of free alkali, and the presence of an equivalent of sodium hydroxide produces complete racemisation at the ordinary temperature in a few hours.

In a recent brief paper, Backer and Mook (*Verslag Akad. Wetenschappen Amsterdam*, 1926, **35**, 737) claim to have obtained aqueous solutions of ammonium *d*- and *l*-chlorobromoacetate displaying a feeble optical activity, the maximum value of $[M]_D$ being $\pm 8°$. We have been unable to establish any such optical activity after repeated fractional separation of the brucine salt from cold water or from alcohol (compare also J., 1926, 2183); moreover, since it is reported that an aqueous solution of the slightly active ammonium chlorobromoacetate containing an equivalent of sodium hydroxide failed to racemise in 24 hours, the optical stability of chlorobromoacetic acid would appear to be even greater than that of chloroiodoacetic acid, a conclusion which is opposed to our current views.

EXPERIMENTAL.

Preparation of Chloroiodoacetic Acid.—The acid was made by the method of Crompton and Carter (J., 1923, **123**, 576), with the following modifications. Upon keeping the mixture of iodine

* In presenting these results for publication we acknowledge our indebtedness to Professor Holland Crompton, through whose courtesy we were enabled to inaugurate the experiments concerned, subsequent to the preparation by him of optically active specimens of ammonium chloroiodoacetate.

monochloride and αβ-dichlorovinyl ethyl ether for 3 weeks (*loc. cit.*), iodine was often liberated to such an extent that very little chloroiodoacetyl chloride remained. Excellent yields were obtained, however, on warming the reaction mixture to 50° after keeping it for 30 minutes only. Upon then removing the solid iodine by filtration and treating the crude chloroiodoacetyl chloride with the calculated amount of water, hydrolysis was found to be complete within about 4 hours, as indicated by solidification. The yield of the acid was finally enhanced by washing the crude product forthwith with light petroleum, prior to recrystallising the almost colourless residue from this solvent.

Following the preparation of chlorobromoacetic acid from chlorobromomalonic acid (J., 1926, 2183), several unsuccessful attempts were made to prepare chloroiodoacetic acid from halogenated malonic or acetic acids, or their esters, by treatment with sodium or potassium iodide in presence of alcohol, ether, or acetone (compare *Ber.*, 1893, **26**, 596; 1910, **43**, 1528). Direct iodination in aqueous or alcoholic solution also proved to be impracticable. Attempts to chlorinate or brominate iodoacetic acid, using sulphuryl chloride and bromine, respectively, in presence of dry ether, likewise resulted in the liberation of iodine. Incidentally, it was not found possible to prepare iodoacetic acid satisfactorily in accordance with the accepted method of heating monochloroacetic acid with potassium iodide in presence of absolute alcohol (compare Sudborough and James, "Practical Organic Chemistry," 1915, p. 118). The yield of the purified acid was increased sevenfold by using acetone in place of alcohol; moreover, the irritating vapour produced in the first method appears to consist mainly of ethyl iodoacetate.

Resolution of Chloroiodoacetic Acid with l-*Hydroxyhydrindamine.*—Hot methyl-alcoholic solutions of the acid (10 g. in 200 c.c.) and base (6·7 g. in 200 c.c.) were mixed in a shallow dish and evaporated to dryness at once, whilst cooling, in a brisk current of air. The residual mass of almost colourless, silky needles was redissolved in the minimum quantity of hot methyl alcohol, diluted considerably with ethyl acetate, and rapidly concentrated on the water-bath until crystallisation occurred readily when the solution was cooled and stirred. Two successive fractions had $[\alpha]_D$ — 32·4° in aqueous solution ($c = 1{\cdot}00$). Upon recrystallisation from the same solvent, separation occurred more readily than from the original solution, and a constant value of $[\alpha]_D$ — 34·0°, $[M]_D$ — 126°, was readily attained for pure l-*hydroxyhydrindamine* l-*chloroiodoacetate* in dilute aqueous solution ($c = 1{\cdot}00$). The salt forms brittle transparent prisms, m. p. 149° (decomp.); it dissolves readily in water or in

warm methyl alcohol, sparingly in acetone, and is practically insoluble in ethyl acetate or chloroform (Found: Cl + I, 43·6. $C_{11}H_{13}O_3NClI$ requires Cl + I, 44·0%). The solutions in organic solvents darken when kept. Aqueous solutions exhibited no mutarotation, and only a very slight decrease in rotatory power was observed after evaporating such solutions to dryness. A distinct downward mutarotation occurred in methyl-alcoholic solution ($c = 1·20$), the value of $[M]_D$ declining from $-135°$ to $-103°$ in 5 days; at the same time, the solution gradually developed a brown colour, indicative of decomposition. A solution in glacial acetic acid decomposed much more rapidly, with liberation of iodine. In chloroform containing a little methyl alcohol, the salt gave $[\alpha]_D - 32·0°$, $[M]_D - 118°$ ($c = 0·67$). Upon treatment with the requisite quantity of brucine acetate in hot methyl alcohol, it yielded brucine *l*-chloroiodoacetate, having $[\alpha]_D - 22·0°$ in methyl alcohol ($c = 0·60$); when this salt was decomposed in the cold with ammonia, the resulting ammonium *l*-chloroiodoacetate had $[\alpha]_D - 24·4°$, $[M]_D - 58°$ in aqueous solution ($c = 2·75$).

The mother-liquor from the original separation of *l*-hydroxyhydrindamine *l*-chloroiodoacetate became very dark; after most of the solvent had evaporated, the residual oily mass was induced to crystallise by treatment with light petroleum. Further treatment with ether yielded two fractions, having $[\alpha]_D - 5·9°$ and $- 2·0°$, and $[M]_D - 22°$ and $- 7°$, respectively, in aqueous solution ($c = 1·00$). The second fraction, composed of minute, feathery needles, appeared to consist of almost pure l-*hydroxyhydrindamine* d-*chloroiodoacetate*, the calculated value for the molecular rotation of the corresponding acid ion in dilute aqueous solution being $+ 53·5°$. The brucine salt precipitated from the mixed fractions was fractionally recrystallised from hot water, and the final fraction, having $[\alpha]_D + 14·0°$ in methyl alcohol ($c = 0·60$), when decomposed in the usual way with dilute ammonia yielded an optically impure ammonium *d*-chloroiodoacetate having $[\alpha]_D + 16·0°$, $[M]_D + 38°$ in aqueous solution ($c = 2·00$).

Resolution of dl-*Chloroiodoacetic Acid with Brucine.*—1. The crude brucine salt, obtained by mixing the components in warm methyl alcohol, had $[\alpha]_D - 9·7°$ in methyl alcohol ($c = 0·60$). Recrystallisation from warm methyl alcohol gave two successive fractions yielding specimens of ammonium chloroiodoacetate with $[\alpha]_D - 2°$ and $+ 1°$, respectively, in dilute aqueous solution.

2. Following preliminary experiments on fractional precipitation with brucine in accordance with the method of Pope and Read (J., 1914, **105**, 817), a warm aqueous solution of ammonium *dl*-chloroiodoacetate (4·4 g. of acid in 300 c.c.) was treated with a

similar solution of one-quarter the calculated weight of brucine hydrochloride (2·3 g. of base in 75 c.c.). After the crystalline brucine salt had been separated from the cold liquid, the filtrate was treated thrice in succession in an exactly similar way with fresh quantities of brucine, the volume of the solution being kept practically constant by evaporation on the water-bath after each filtration. The four fractions of brucine salt had roughly the same weight (2·75 g.), and the respective values of $[\alpha]_D$ in methyl alcohol ($c = 0{\cdot}60$) were $-22°$, $-8°$, $+6°$, and $+8°$. After two recrystallisations from water containing a little methyl alcohol, the first fraction gave, upon decomposition with ammonia, a specimen of ammonium *l*-chloroiodoacetate having $[\alpha]_D - 25{\cdot}1°$, $[M]_D - 60°$, in water ($c = 2{\cdot}11$). Further observations indicated that this specimen of ammonium *l*-chloroiodoacetate was optically pure. An aqueous solution of ammonium *l*-chloroiodoacetate (6·53 g. in 250 c.c.) having $[M]_D - 32°$, prepared from a number of intermediate fractions of the brucine salt which had accumulated in several series of operations, was treated in the usual way with two successive quantities of one-quarter the calculated amount of brucine hydrochloride. The two specimens of ammonium *l*-chloroiodoacetate obtained by decomposing the ensuing fractions of brucine *l*-chloroiodoacetate had the respective values $[\alpha]_D - 25{\cdot}0°$, $[M]_D - 59°$, and $[\alpha]_D - 24{\cdot}4°$, $[M]_D - 58°$ in 3% aqueous solution. The two specimens were then mixed and treated once again with one-quarter the calculated amount of brucine hydrochloride under the usual conditions: the resulting brucine salt, when decomposed in the cold with dilute ammonia, yielded ammonium *l*-chloroiodoacetate having $[\alpha]_D - 25{\cdot}0°$, $[M]_D - 59°$. The corresponding pure, air-dried *brucine* l-*chloroiodoacetate* had $[\alpha]_D - 22{\cdot}0°$ in methyl alcohol ($c = 0{\cdot}60$); this salt forms small, glistening prisms, m. p. 158—160° (decomp.), which dissolve very sparingly in hot water and readily in warm methyl alcohol.

After the addition of one-half the calculated amount of brucine hydrochloride to a hot aqueous solution of ammonium *dl*-chloroiodoacetate, the succeeding fractions of the brucine salt usually exhibit a low dextrorotation in methyl alcohol; the fractions are also more readily soluble and consist of large, glistening prisms. A fraction of the brucine salt having $[\alpha]_D + 6°$ in methyl alcohol yielded ammonium *d*-chloroiodoacetate having $[\alpha]_D + 17{\cdot}5°$, $[M]_D + 42°$, in 4% aqueous solution. After the original brucine salt had been recrystallised three times from hot water, the corresponding ammonium *d*-chloroiodoacetate had $[\alpha]_D + 15{\cdot}0°$, $[M]_D + 36°$. Fractional precipitation of this salt with one-half the calculated quantity of brucine gave an ammonium salt having

$[\alpha]_D$ + 15·8°, $[M]_D$ + 38°. Prolonged evaporation of aqueous solutions of brucine *d*-chloroiodoacetate on the water-bath appears to bring about partial racemisation of the acid component of the salt.

3. The preparation of optically pure brucine *d*-chloroiodoacetate by the normal methods of fractional crystallisation or fractional precipitation is thus difficult; success was achieved, however, by conducting the second of these operations from a solution having about 3·5 times the concentration noted in paragraph (2) above. Two aqueous solutions were prepared, each of 500 c.c.; these contained, respectively, 22·0 g. of *dl*-chloroiodoacetic acid as ammonium salt and 46·6 g. of brucine in the form of hydrochloride. Upon rapidly adding a portion (150 c.c.) of the hot brucine solution to the whole of the first solution on the water-bath, crystallisation began about one minute after mixing and continued rapidly. The fraction (19·8 g.) collected by filtering the cold mixture consisted of practically pure *brucine* d-*chloroiodoacetate*. This had $[\alpha]_D$ + 21·0° in methyl alcohol (c = 0·60); 0·7647 g. of the corresponding ammonium *d*-chloroiodoacetate contained in 20·0 c.c. of aqueous solution gave α_D + 1·80° in a 2-dcm. tube, whence $[\alpha]_D$ + 23·5° and $[M]_D$ + 56°. A second fraction of brucine salt, yielded similarly by the filtrate from the first fraction, gave a specimen of ammonium *l*-chloroiodoacetate having $[M]_D$ − 32°. Both these fractions of brucine salt were allowed to separate spontaneously without inoculation. Further experiments indicated that the character of the crystalline separation may be controlled to some extent by seeding the supersaturated solution in such instances with specimens of brucine *l*- or *d*-chloroiodoacetate; it is proposed to submit this interesting aspect of the investigation to fuller inquiry.

Ammonium l- *and* d-*Chloroiodoacetate*.—The ammonium salts were prepared by shaking cold aqueous suspensions of the corresponding brucine salts with the calculated amounts of a standard solution of ammonia in presence of chloroform, the ammonia being added in small portions. Traces of brucine were finally removed from the aqueous layer by two further extractions with chloroform. After the value of α_D in a 2-dcm. tube had been observed for the resulting aqueous solution of the ammonium salt, an aliquot portion of the solution was evaporated to dryness on the water-bath in order to determine the concentration. The highest values observed for ammonium *l*- and *d*-chloroiodoacetate were $[\alpha]_D$ − 25·1°, $[M]_D$ − 60°, and $[\alpha]_D$ + 23·5°, $[M]_D$ + 56°, respectively, in dilute aqueous solution as recorded above. The salts form colourless, glistening needles (decomp. 149—150°), which usually become yellow and then brown when kept for a few days in a desiccator (Found: NH_3, 7·2.

$C_2H_5O_2NClI$ requires NH_3, 7·2%). It is thus advisable to keep the active acids in the form of their brucine salts. Crystalline ammonium *l*-chloroiodoacetate having $[\alpha]_D$ — 25·1°, $[M]_D$ — 60°, after being kept for 10 days in a desiccator, gave $[\alpha]_D$ — 24·6°, $[M]_D$ — 58° in aqueous solution ($c = 0·50$) and $[\alpha]_D$ — 24·4°, $[M]_D$ — 57° in methyl alcohol ($c = 0·75$).

No appreciable racemisation was noticed upon evaporating 5 c.c. of a 3·76% aqueous solution of ammonium *d*-chloroiodoacetate, having $[\alpha]_D$ + 19·0°, to dryness on the water-bath. Sustained evaporation of larger volumes, however, produced a noticeable decline in the rotatory power; a slow decline occurred also on keeping aqueous solutions at the ordinary temperature for long periods.

Upon dissolving 0·2116 g. of ammonium salt having $[M]_D$ — 58° in 20·0 c.c. of water containing 2 c.c. of 2*N*-ammonia and evaporating the solution to dryness on the water-bath, the recovered salt had $[\alpha]_D$ — 10·4°, $[M]_D$ — 25°. Further, 0·2200 g. of ammonium salt having $[\alpha]_D$ — 24·1° was dissolved in water containing an equivalent of sodium hydroxide and made up to 20·0 c.c.; the value of α_D in a 2-dcm. tube after 30 minutes was — 0·50°, and when kept for 24 hours at the ordinary temperature the solution had become optically inactive. No appreciable removal of halogen by hydrolysis was detected at the end of this time. In a similar experiment the value of α_D declined over-night from — 0·68° to zero.

An aqueous solution of 0·1882 g. of ammonium salt having $[\alpha]_D$ + 19·0°, $[M]_D$ + 44°, was made up to 20·0 c.c. with water containing one equivalent of hydrochloric acid. The resulting value of α_D in a 2-dcm. tube was + 0·15°, whence the free acid under these conditions has $[\alpha]_D$ + 0·9°, $[M]_D$ + 2°.

The authors are indebted to the Department of Scientific and Industrial Research for a maintenance grant and to the Carnegie Trust for a Fellowship which enabled one of them (A. M. M.) to take part in this work. The investigations are being continued.

United College of St. Salvator and St. Leonard,
University of St. Andrews. [*Received, January 7th*, 1927.]

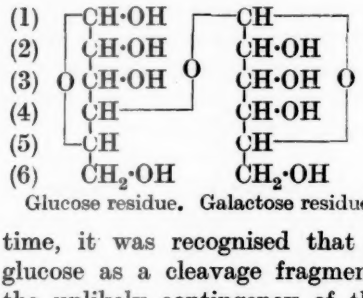
LXXXI.—*The Constitution of the Disaccharides. Part XII. Lactose.*

By WALTER NORMAN HAWORTH and CHARLES WILLIAM LONG.

THE constitutional study of lactose (Haworth and Leitch, J., 1918, **113**, 188) showed that from completely methylated lactose the products of hydrolytic cleavage were crystalline 2 : 3 : 6-trimethyl glucose and normal tetramethyl galactose, and a structural formula was applied to lactose on this experimental basis. These results have since been experimentally verified by Irvine and Hirst (J., 1922, **121**, 1213) and by Schlubach and Moog (*Ber.*, 1923, **56**, 1957).

In the subsequent communication in which the evidence for a complete revision of the structure of normal glucose was outlined—a revision which extended also to all carbohydrates containing glucose residues—it was shown that derivatives of normal glucose should be represented by an amylene-oxide ring structure (Charlton, Haworth, and Peat, J., 1926, 89). In the latter paper, therefore, the constitutional formula previously applied to lactose and cellobiose was revised by the introduction of the above emendation. This involved the change from a butylene-oxide structure to the new amylene-oxide formulation in each of the hexose residues, and also a corresponding adjustment in the point of attachment of the biose linking from position 5 to position 4.

(I.)



Glucose residue. Galactose residue.

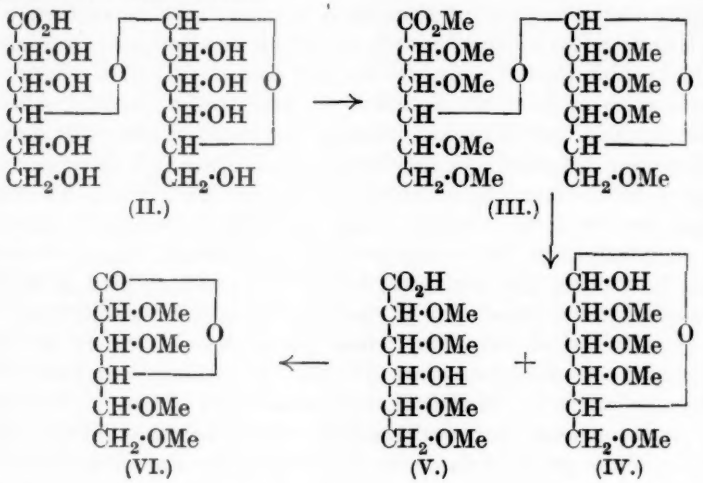
At the same time, it was recognised that the isolation of 2 : 3 : 6-trimethyl glucose as a cleavage fragment of methylated lactose left open the unlikely contingency of the presence of a butylene-oxide ring or γ-sugar residue in the reducing half of the disaccharide, since the positions 4 and 5 were available either for the allocation of an oxide-ring attachment or for the position of the biose linking. The reason for suspending final judgment in regard to this contingency was fully explained. It was pointed out that crystalline 2 : 3 : 6-trimethyl glucose, although itself an amylene-oxide sugar, could conceivably have originated as a labile butylene-oxide form at the moment of its separation from methylated lactose, and had thereafter undergone

isomeric change into the normal amylene-oxide variety which was isolated. It was recognised, however, that lactose did not itself display the behaviour of a labile or γ-sugar, and consequently we preferred the structural formula (I) which was definitely advanced.

In a subsequent paper, Irvine and Black (J., 1926, 862) took occasion to criticise the formulæ we had applied to the reducing disaccharides, including lactose and cellobiose, the constitutions of which they regarded as conjectural. Following this criticism, two papers have since appeared (G. Zemplén, *Ber.*, 1926, **59**, 1254, 2402) describing the constitutional study of lactose and cellobiose by degradation to the hexose-tetroses, and the experimental results entirely confirm the structural formulæ we had applied to lactose and cellobiose. Inasmuch as exception might be taken, however, to the method of Zemplén, whose proof depends upon the non-formation of phenylosazones by the hexose-tetroses, we have continued our work on the constitutional study of lactose, and have adopted a scheme, herein described, which furnishes, in our view, quite definite proof of the position occupied by the biose linking in this disaccharide; and consequently the nature of the oxide ring also is fully established.

In this experimental work, we oxidised lactose to lactobionic acid, the barium salt of which was methylated, thus giving rise to methyl octamethyl-lactobionate. In this compound it will be seen that the oxide-ring in the reducing hexose residue of the parent disaccharide has been eliminated, and the hydroxyl position thus exposed has been protected by a methyl residue, whilst the biose linking has presumably remained intact. Hydrolysis of this methylated lactobionate should give cleavage products which leave no doubt as to the position of the biose linking, since only one free hydroxyl group would be exposed in the hexonic acid residue resulting from the hydrolysis. On digesting the methyl octamethyl-lactobionate with dilute hydrochloric acid, we were able to isolate crystalline 2 : 3 : 4 : 6-tetramethyl galactose (IV), which had already been recognised in the course of previous work, and also crystalline 2 : 3 : 5 : 6-tetramethyl γ-gluconolactone (VI), identical in every respect with the specimen we had recently isolated in the course of a similar investigation on maltose (Haworth and Peat, J., 1926, 3094). This crystalline lactone gave rise to a crystalline phenylhydrazide of the corresponding 2 : 3 : 5 : 6-tetramethyl gluconic acid (V), and consequently the diagnosis of these two products arising from the cleavage of the methylated lactobionic acid enables us to ascribe a constitutional formula (III) to methyl octamethyl-lactobionate and the formula (II) to lactobionic acid. It therefore follows that the constitution (I) which we had already advanced

and supported in the course of our earlier work receives further experimental verification.



Experimental.

Methylation of Lactobionic Acid. Isolation of Methyl Octamethyllactobionate.—Lactobionic acid was prepared by the oxidation of lactose with bromine water, and the procedure described by Fischer and Meyer (*Ber.*, 1889, **22**, 1941) was adopted as a means of obtaining the calcium and the barium salt. An aqueous solution of the latter salt was gradually added to a large volume of alcohol which was well stirred. Barium lactobionate was precipitated as a colourless, micro-crystalline solid which contained 14·0% of barium. Calcium lactobionate, purified by the same method, contained 4·6% of calcium. It would thus appear that each salt is associated with three molecules of ethyl alcohol, and this seems to be true also of calcium maltobionate. The salts were neutral and devoid of action towards Fehling's solution.

Barium lactobionate was methylated in a manner similar to that already mentioned in the case of calcium maltobionate (Haworth and Peat, *loc. cit.*). After eight treatments with the methylating agents, a preliminary distillation at 0·09 mm. pressure showed little evidence of hydrolytic cleavage. Thus from a total distillate of 16·5 g., only 1·7 g. were collected at a bath temperature of 170—180°, and this first fraction showed $n_D^{13°}$ 1·4561. The main distillate (14·8 g.), a pale yellow, viscid liquid, showed b. p. 178—210°/0·09 mm. and $n_D^{13°}$ 1·4625—1·4689. This was subjected to one methylation with moist silver oxide and methyl iodide, followed by two further treatments with the dry reagents, and at this stage the

material was again distilled. A small first fraction (0·5 g.), which distilled at a bath temperature of 160—180° under 0·08 mm. and had $n_D^{13°}$ 1·4612, having been rejected, the main portion was collected at a bath temperature of 180—185° and distilled at 157—164°/0·05 mm. This specimen of methyl octamethyl-lactobionate, which was devoid of action towards Fehling's solution, showed $n_D^{13°}$ 1·4632 (Found: C, 51·8; H, 8·1; OMe, 54·8. Calc. for $C_{21}H_{40}O_{12}$: C, 52·1; H, 8·3; OMe, 57·6%).

Hydrolysis. The above specimen was hydrolysed in contact with 7·0% hydrochloric acid at 80—90° during 6½ hours. Portions of the solution were examined polarimetrically at intervals: $[\alpha]_D$ (initial), + 34·0°; 72·6° (after 1 hour); 74·5° (2 hours); 76·8° (3 hours); 77·6° (4 hours); 77·6° (5½ hours); 77·2° (6½ hours). The hydrolysis was probably complete after 4 hours, and certainly after 6½ hours; no appreciable change had occurred in the appearance of the solution, which now reduced Fehling's solution.

At this stage, the solution was gently heated in contact with barium carbonate until the whole of the acid product was neutralised. The colourless filtrate was evaporated under diminished pressure, and the dried residue was repeatedly extracted with ether until it no longer gave a positive test with Fehling's solution. From this ethereal extract, colourless crystals of tetramethyl galactose were isolated, showing $[\alpha]_D$ + 118·1° in equilibrium in water (yield, 95%). A mixed melting-point determination of this substance with an authentic specimen of crystalline 2 : 3 : 4 : 6-tetramethyl galactose (compare Haworth, Ruell, and Westgarth, J., 1924, **125**, 2473) gave m. p. 71—72°. Schlubach and Moog (*loc. cit.*) gave m. p. 71·5—72° for the sugar they then described as 2 : 3 : 5 : 6-tetramethyl galactose.

The crystalline anilide was prepared (m. p. 190—191°), and this m. p. was not depressed in admixture with an authentic specimen of 2 : 3 : 4 : 6-tetramethyl galactose anilide (Found: C, 61·7; H, 7·9. Calc.: C, 61·7; H, 8·0%).

Separation of 2 : 3 : 5 : 6-*Tetramethyl* γ-*Gluconolactone.*—The colourless residue of barium salts was dissolved in the minimum of water and the free organic acid was liberated by the cautious addition of *N*/2-hydrochloric acid. Evaporation at 30°/14 mm., followed by a period of heating at 60°/0·09 mm., gave a dried residue containing barium chloride and the organic lactone, from which the latter was extracted by means of dry ether. Evaporation of the ethereal solution furnished a liquid product which was distilled under 0·03 mm. at a bath temperature of 117—135°. The cooled distillate was nucleated with a specimen of crystalline 2 : 3 : 5 : 6-tetramethyl γ-gluconolactone prepared by oxidation of 2 : 3 : 5 : 6-tetramethyl γ-glucose, and thereafter it crystallised completely

(m. p. 26—28°), and a mixture of this substance with an authentic specimen obtained in the course of recent work on the hydrolysis of methyl octamethylmaltobionate (Haworth and Peat, *loc. cit.*) melted at 26—27·5° (yield, 90% of the theoretical).

The phenylhydrazide was prepared as colourless, silky needles, m. p. 136° (remelted at 135—136°). Also the m. p. of a mixture of this specimen with that prepared by Haworth and Peat (*loc. cit.*) from methyl octamethylmaltobionate showed no depression (Found by micro-analysis: C, 56·35; H, 7·6; OMe, 34·1. Calc.: C, 56·1; H, 7·6; OMe, 36·3%).

The authors gratefully acknowledge a maintenance grant to one of them from the Department of Scientific and Industrial Research.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, January 22nd,* 1927.]

LXXXII.—*A New Synthesis of Oxyberberine and a Synthesis of Palmatine.**

By ROBERT DOWNS HAWORTH, JOSEPH BLAKE KOEPFLI, and WILLIAM HENRY PERKIN, jun.

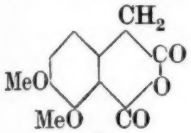
THE general method devised for the synthesis of the berberine type of alkaloid (Haworth, Perkin, and Pink, J., 1925, **127**, 1709) has been applied to the synthesis of *epi*berberine and of 2 : 3 : 9 : 10-bismethylenedioxyprotoberberine † by utilising 3 : 4-methylenedioxyhomophthalic acid (Haworth and Perkin, J., 1926, 1769) as the starting point.

The present communication describes the preparation of 3 : 4-*dimethoxyhomophthalic anhydride* (I) and the use of this substance in the synthesis of oxyberberine and palmatine. 3 : 4-Dimethoxyhomophthalic anhydride (I) was prepared by a slight modification of the method used in the preparation of 3 : 4-methylenedioxyhomophthalic acid (Haworth, Perkin, and Stevens, J., 1926, 1764). β-Veratrylpropionic acid was brominated and the β-6-*bromoveratrylpropionic acid* converted into 4-*bromo*-6 : 7-*dimethoxy*-1-*hydrindone* (II) by treatment with concentrated sulphuric acid. The iso*nitroso*-derivative was prepared in the usual manner and treated with

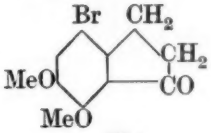
* Compare Späth and Quietensky (*Ber.*, 1925, **58**, 2267).

† Kitasato (*Proc. Imp. Acad. Tokyo*, 1926, **2**, 124) has recently isolated an alkaloid from *Coptis japonica*, which he has named coptisine. This alkaloid appears to be identical with 2 : 3 : 9 : 10-bismethylenedioxyprotoberberine, obtained as an intermediate stage in the synthesis of protopine (Haworth and Perkin, *loc. cit.*, p. 1783).

toluene-*p*-sulphonyl chloride in alkaline solution, and the resulting *6-bromo-2-carboxy-3 : 4-dimethoxyphenylacetonitrile* was hydrolysed to *6-bromo-3 : 4-dimethoxyhomophthalic acid* (III). This acid was debrominated in alkaline solution with sodium amalgam, and the crude 3 : 4-dimethoxyhomophthalic acid converted into its *anhydride* (I) by the action of acetyl chloride.



(I.)



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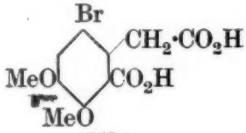
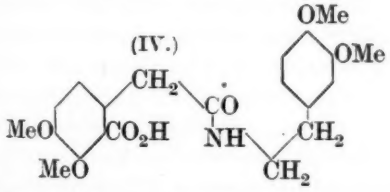
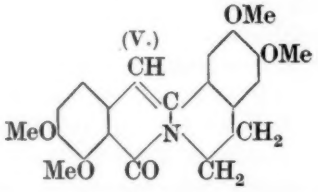


(III.)

In order to establish the constitution of the anhydride (I), and the possibility of its application to the syntheses of substances of the berberine type, it was first condensed with β-piperonylethylamine, the resulting unpurified amic acid esterified, the crude methyl ester boiled with phosphorus oxychloride, and the resulting oxyberberine identified by comparison with a specimen obtained by the action of sodium hydroxide on berberinium chloride.

For the synthesis of palmatine, 3 : 4-dimethoxyhomophthalic anhydride (I) was condensed with β-veratrylethylamine, and *N-β-veratrylethyl-3 : 4-dimethoxyhomophthalamic acid* (IV) was obtained as a gum which so far has not been crystallised. The *methyl* ester, prepared from the silver salt of the acid (IV), was converted by treatment with phosphorus oxychloride into a substance, $C_{21}H_{21}O_5N$, m. p. 183°, which exhibited the properties characteristic of a substance of the oxyberberine type. There can be no doubt that this substance is *oxypalmatine* (V), which does not appear to have been previously described. The oxypalmatine was reduced electrolytically and thus converted into a base, m. p.

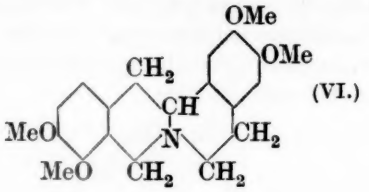




147°, which was identical with a specimen of tetrahydropalmatine (VI) obtained by reducing palmatine iodide. The synthetical tetrahydropalmatine was next oxidised by iodine to a bright yellow iodide and this was identical with a specimen of palmatine iodide (VII) obtained from the natural alkaloid.*

* Professor E. Späth was kind enough to furnish us with a sample of palmatine iodide of natural origin, which made direct comparison possible.

The authors are continuing these researches with a view to the synthesis of the ten-membered ring alkaloid (VIII).



(VI.)

(VII.)

I

(VIII.)

EXPERIMENTAL.

β-6-*Bromoveratrylpropionic Acid.*—Bromine (1¼ mols.), dissolved in glacial acetic acid (1 part), was gradually added with shaking and cooling to β-veratrylpropionic acid (1 mol.) in glacial acetic acid (2 parts). The bromo-acid rapidly separated, and, after remaining for 12 hours, the mixture was diluted with water and the acid was collected and dried; it recrystallised from benzene in colourless prisms, m. p. 118—119° (yield, 90% of the theoretical) (Found: C, 46·0; H, 4·5. $C_{11}H_{13}O_4Br$ requires C, 45·7; H, 4·5%).

4-*Bromo*-6 : 7-*dimethoxy*-1-*hydrindone* (II).—β-6-Bromoveratrylpropionic acid (10 g.) was dissolved in concentrated sulphuric acid (50 c.c.) at 75°, and maintained at this temperature for 5 minutes. The deep red solution was poured into ice and extracted with chloroform; the extract was washed with aqueous sodium carbonate and dried, and the solvent removed.* The residual oil, which solidified on rubbing, crystallised from methyl alcohol in almost colourless needles (2·5 g.), m. p. 120—121° (Found: C, 48·5; H, 4·0. $C_{11}H_{11}O_3Br$ requires C, 48·7; H, 4·1%). The *oxime*, prepared by the action of hydroxylamine hydrochloride and potassium acetate on an alcoholic solution of the bromohydrindone (II), is sparingly soluble in ethyl alcohol, from which it crystallises in colourless prisms, m. p. 228—230° (Found: N, 4·7. $C_{11}H_{12}O_3NBr$ requires N, 4·8%).

4-*Bromo*-2-iso*nitroso*-6 : 7-*dimethoxy*-1-*hydrindone*.—The bromo-

* In attempts to prepare the hydrindone (II) on a larger scale, debromination occurred to a considerable extent, resulting in the formation of a mixture of the bromohydrindone (II) and 5 : 6-dimethoxy-1-hydrindone.

hydrindone (II) (2 g.), dissolved in the minimum of methyl alcohol containing concentrated hydrochloric acid (3 c.c.), was saturated with methyl nitrite; the precipitated iso*nitroso*-derivative crystallised from ethyl alcohol in slender, elongated, pale yellow prisms (2 g.), m. p. 236° (decomp.) (Found: C, 44·2; H, 3·4. $C_{11}H_{10}O_4NBr$ requires C, 44·0; H, 3·3%).

6-*Bromo*-2-*carboxy*-3 : 4-*dimethoxyphenylacetonitrile*. — The *iso*-nitrosohydrindone (2 g.) in aqueous sodium hydroxide (18 c.c. of 8%) was gradually treated with toluene-*p*-sulphonyl chloride (2 g.) with shaking, and solution completed by raising the temperature to 80°. When the mixture was cooled, filtered, and acidified with hydrochloric acid, the *nitrile* separated as an oil, which solidified on rubbing and crystallised from much boiling water in almost colourless needles, containing $1H_2O$, m. p. 98—100° (Found: loss at 100°, 5·1. Calc. for $1H_2O$, 5·6%. Found in material dried at 100°: C, 43·5; H, 3·6. $C_{11}H_{10}O_4NBr$ requires C, 44·0; H, 3·3%).

6-*Bromo*-3 : 4-*dimethoxyhomophthalic Acid* (III).—Crude 6-bromo-2-carboxy-3 : 4-dimethoxyphenylacetonitrile was boiled with sodium hydroxide solution (8%) until evolution of ammonia had ceased. The solution was acidified with dilute hydrochloric acid, extracted several times with ether and dried, the ether removed, and the residual light brown gum refluxed with a slight excess of acetyl chloride for ½ hour. After evaporation under reduced pressure, the *anhydride* separated, and crystallised from benzene in very pale yellow, glistening plates, m. p. 151° (Found: C, 44·0; H, 3·0. $C_{11}H_9O_5Br$ requires C, 43·9; H, 3·0%). 6-*Bromo*-3 : 4-*dimethoxyhomophthalic acid* (III) was obtained by hydrolysing the above anhydride with sodium hydroxide solution (8%), acidifying the mixture with hydrochloric acid, extracting it with ether, drying the extract and removing most of the solvent, adding benzene, and removing the remaining ether. The acid (III) slowly separated in colourless prisms, m. p. 166—167°, which were readily soluble in water and ether but sparingly soluble in benzene (Found: C, 41·4; H, 3·4. $C_{11}H_{11}O_6Br$ requires C, 41·6; H, 3·5%).

3 : 4-*Dimethoxyhomophthalic Anhydride* (I).—Pure bromodimethoxyhomophthalic anhydride (5 g.) was dissolved in sodium hydroxide solution (8%), diluted with water, and heated on the water-bath for 12 hours with sodium amalgam (150 g. of 4%). The solution was cooled, filtered, acidified, and extracted several times with ether, the extract dried, the ether removed, and the residual brown oil, consisting of 3 : 4-dimethoxyhomophthalic acid, converted into 3 : 4-*dimethoxyhomophthalic anhydride* (I) by boiling with acetyl chloride, which was then evaporated under reduced pressure. The

anhydride separated from dry benzene in almost colourless plates, m. p. 104—105°, which became sticky on long standing owing to absorption of water (Found : C, 59·6; H, 4·5. $C_{11}H_{10}O_5$ requires C, 59·5; H, 4·5%). A crystalline specimen of 3 : 4-dimethoxyhomophthalic acid has not yet been obtained.

Oxyberberine.—A benzene solution of 3 : 4-dimethoxyhomophthalic anhydride (I) (1·1 g.) and β-piperonylethylamine (from 2·0 g. of the hydrochloride) was refluxed for 1 hour, the solution extracted with aqueous sodium hydroxide (8%), the alkaline layer acidified, the precipitated oily amic acid extracted with chloroform and dried, and the solvent removed. The residual gum (1·5 g.) was dissolved in water containing sodium bicarbonate (0·35 g.), and the filtered solution was treated with silver nitrate (1·0 g.). After remaining over-night, the precipitated silver salt was collected, successively washed with water, methyl alcohol, and ether, dried, powdered, suspended in ether, and refluxed for 12 hours with excess of methyl iodide. After filtering from the silver salts, the ether was removed, and the residual gum boiled with phosphorus oxychloride for 5 minutes, forming a red solution. The excess of the oxychloride was removed under reduced pressure, and the residue was diluted with hot water, treated with charcoal, and filtered. The filtrate was made alkaline with sodium hydroxide, the amorphous precipitate extracted with chloroform, the solvent removed from the extract, and the residue digested for some time with dilute hydrochloric acid; the solid obtained crystallised from glacial acetic acid, containing a little water, in pale yellow needles, m. p. 197·5°. After three successive crystallisations from alcohol, xylene, and alcohol, pale yellow needles (0·15 g.), m. p. 198—200°, were obtained, which showed no depression in m. p. when mixed with a specimen of oxyberberine prepared by the action of sodium hydroxide on berberinium chloride. The colour reactions of the synthetical product corresponded with those exhibited by oxyberberine.

N-β-*Veratrylethyl*-3 : 4-*dimethoxyhomophthalamic Acid* (IV).—3 : 4-Dimethoxyhomophthalic anhydride (I) (1·2 g.) and β-veratrylethylamine (1·0 g.) were refluxed for 3 hours in benzene (10 c.c.), and the product was extracted with sodium hydroxide solution (5%), the alkaline layer acidified, the precipitated light brown oil extracted with chloroform, the extract dried, and the solvent removed. The residual oil (2·0 g.) was dissolved in water, containing sodium bicarbonate (0·5 g.), and treated with excess of silver nitrate. After 12 hours, the precipitated silver salt was collected, washed successively with water, methyl alcohol, and ether, dried in a desiccator, powdered, suspended in ether, and refluxed

with excess of methyl iodide for 12 hours. After filtering from silver salts, the ethereal solution was concentrated; the crystalline *methyl* ester, m. p. 90—94°, obtained recrystallised from ether in colourless plates, m. p. 93—94° (Found: C, 63·4; H, 6·5. $C_{22}H_{27}O_7N$ requires C, 63·3; H, 6·4%). It is soluble in most organic solvents with the exception of light petroleum.

Oxypalmatine (V).—The methyl ester was boiled with phosphorus oxychloride for 10 minutes, and the dark red solution concentrated under diminished pressure. A solution of the residue in boiling water was treated with charcoal, filtered, and made alkaline with sodium hydroxide, and the precipitate was extracted with chloroform. The extract was dried, the chloroform removed, and the residue digested with dilute hydrochloric acid; the crystalline solid obtained recrystallised from methyl alcohol in buff-coloured prisms, m. p. 183° (Found: C, 68·8; H, 5·6. $C_{21}H_{21}O_5N$ requires C, 68·6; H, 5·7%).

Oxypalmatine dissolves in glacial acetic acid and is precipitated by addition of water, and its solution in ethyl alcohol or benzene exhibits a bluish-violet fluorescence. When it is treated with sulphuric acid (50%), a sparingly soluble, bright yellow *sulphate* separates and the addition of a drop of concentrated nitric acid produces an intense violet coloration.

Tetrahydropalmatine (VI).—Oxypalmatine (1 g.), dissolved in methyl alcohol (60 c.c.) and concentrated sulphuric acid (40 c.c.), was reduced in an electrolytic cell with a current of 4½ amps. for 18 hours with water-cooling and for a further 6 hours without cooling. The almost colourless solution was diluted with an equal volume of water, treated with charcoal, filtered, made alkaline with ammonia, and extracted with chloroform, and the extract was dried and the solvent removed. The residue, consisting of crude tetrahydropalmatine, was converted into the sparingly soluble hydrochloride by the action of a little dilute hydrochloric acid. The hydrochloride was collected, dissolved in hot water, and treated with sodium hydroxide; the amorphous base thus obtained crystallised from methyl alcohol in colourless, rhombic plates, m. p. 147° (Found: C, 71·2; H, 7·1. Calc. for $C_{21}H_{25}O_4N$: C, 71·0; H, 7·0%). A specimen of tetrahydropalmatine was prepared by reducing palmatine iodide with zinc dust and dilute sulphuric acid, and no alteration was observed in the melting point of a mixture of this and the synthetical base.

Palmatine Iodide (VII).—Synthetical tetrahydropalmatine (0·1 g.), dissolved in ethyl alcohol, was oxidised by boiling it with an excess of alcoholic iodine in the presence of potassium acetate. The red periodide which rapidly separated was collected, washed

with ethyl alcohol, suspended in much boiling water, and decomposed with sulphurous acid, and the solution obtained was filtered and cooled. The sparingly soluble palmatine iodide separated in long, orange-yellow needles, m. p. 241° (decomp.), and showed no depression in melting point when mixed with a specimen of palmatine iodide sent us by Professor E. Späth.

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OXFORD.

[*Received, February 3rd,* 1927.]

LXXXIII.—*Aromatic Thionyl and Chlorothionyl Derivatives. Part II.* 1 : 2- *and* 2 : 3-*Thionyldihydroxyanthracenes.*

By ALBERT GREEN.

PHENOLIC thionyl derivatives have been classified (this vol., p. 500) according to their behaviour with weak organic acids. In the present paper, the thionyl derivatives of dihydroxyanthracenes are compared with those of the corresponding dihydroxyanthraquinones (J., 1924, **125**, 1450; 1926, 2198).

1 : 2-Dihydroxyanthracene is obtainable from 1 : 2-dihydroxyanthranol (deoxyalizarin) by Perkin's reduction method (J., 1923, **123**, 2029).

2 : 3-Dihydroxyanthracene has been described, as straw-yellow plates darkening at 180° and melting at about 192°, by Lagodinski (*Annalen*, 1905, **342**, 106), who obtained it by boiling its dimethyl ether with hydriodic acid. The diacetyl derivative melted at 155—160°. The present author prepared 2 : 3-dihydroxyanthracene from hystazarin by the two-stage reduction method (stannous chloride followed by the aluminium–mercury couple) used by Perkin (*loc. cit.*, pp. 2029, 2606) in the preparation of other hydroxyanthracenes from the hydroxyanthraquinones. The properties of the intermediate anthranol so obtained agreed with those ascribed to it by Schrobsdorff (*Ber.*, 1903, **36**, 2938), who reduced hystazarin by means of zinc dust and ammonia. 2 : 3-Dihydroxyanthranol, on reduction by the couple, gave a product, m. p. 282°, whose diacetyl derivative melted at 175°. These properties do not agree with those of Lagodinski's substance, but confirmation of the new product as 2 : 3-dihydroxyanthracene was obtained by analyses, by molecular-weight determinations, and by the oxidation of the acetyl derivative to diacetylhystazarin. The colour reactions of the compound described herein conform substantially with those of Lagodinski's substance, and the probability of the latter having

been obtained in a very impure state is supported by the indefinite melting point and the yellow colour ascribed to the acetyl derivative.

Unfortunately, all attempts to prepare the dimethyl ether from 2 : 3-dihydroxyanthracene were fruitless, although methyl sulphate, diazomethane, and hydrolysis of the diacetyl derivative by sulphuric acid and by hydrogen chloride in absolute methyl-alcoholic solution were resorted to. Similar resistance of other dihydroxyanthracenes to etherification has been noted by Perkin (*loc. cit.*, p. 2035). Lagodinski prepared his 2 : 3-dimethoxyanthracene from veratrole and phthalic anhydride through *o*-3′ : 4′-dimethoxybenzoylbenzoic acid.

1 : 2- and 2 : 3-*Thionyldihydroxyanthracenes* were obtained by the interaction of the hydroxy-compounds and thionyl chloride in pyridine–carbon disulphide solution. They are remarkably stable to moisture, remaining unchanged after 6 weeks' contact with moist air; thionylalizarin (*loc. cit.*) completely reverts to alizarin on standing in air over-night. Both thionyl compounds are decomposed to the dihydroxyanthracenes by solution in cold concentrated sulphuric acid or in cold aqueous caustic alkali.

1 : 2-Thionyldihydroxyanthracene shows no signs of reacting with acetic acid until this boils; complex decomposition then occurs and sulphur and sulphur dioxide are produced. This unexpectedly complex reaction may be accounted for by the proximity of the reaction temperature to the m. p. of the thionyl compound, which darkens at 125° and melts at 138—139° (decomp.). A similar reaction occurs when it is heated with acetic acid and pyridine.

2 : 3-Thionyldihydroxyanthracene differs from thionylhystazarin (*loc. cit.*) in not reacting with boiling acetic acid. When a trace of pyridine is added to the solution, decomposition proceeds slowly with evolution of sulphur dioxide and formation of 2 : 3-dihydroxyanthracene. This "hydroxylic decomposition" corresponds with that of thionylhystazarin. 2 : 3-Thionyldihydroxyanthracene is quantitatively converted into 2 : 3-diacetoxyanthracene by acetic anhydride and pyridine.

EXPERIMENTAL.

1 : 2-*Dihydroxyanthracene.*—The crude reduction product from deoxyalizarin was acetylated, and the purified diacetyl derivative was hydrolysed in small quantities (1 to 2 g.) by means of acetic and hydrochloric acids (Perkin, *loc. cit.*). This tedious process appears to provide the best means of obtaining pure 1 : 2-dihydroxyanthracene in faintly green plates, m. p. 160—161° (Found: C, 79·8; H, 4·9. Calc.: C, 80·0; H, 4·8%).

2 : 3-*Dihydroxyanthracene*.—Hystazarin was recovered practically unchanged after attempts to reduce it directly to 2 : 3-dihydroxyanthracene by the aluminium–mercury couple, alcohol and ammonia.

(a) 2 : 3-*Dihydroxyanthranol*. Finely-divided, moist hystazarin, obtained by hydrolysis of its pure diacetate (compare J., 1926, 2199) with sulphuric acid, when boiled with a hydrochloric acid solution of stannous chloride until a test portion, dissolved in excess of caustic soda, showed a light greenish-yellow colour, gave a quantitative yield of the anthranol, which crystallised from alcohol in bunches of small, yellowish-brown rods, m. p. 288—289° (Schrobsdorff, *loc. cit.*, gives m. p. 282°) (Found : C, 74·2; H, 4·4. Calc. : C, 74·3; H, 4·4%). Its aqueous and alcoholic solutions give an olive-green colour with ferric chloride, and the other colour reactions correspond with those described by Schrobsdorff.

The triacetyl derivative, prepared by means of acetic anhydride and pyridine, formed white, hair-like needles (from alcohol), m. p. 164° (Found : CH_3·CO, 36·8. Calc. : CH_3·CO, 36·6%).

(b) 2 : 3-*Dihydroxyanthracene*. The crude damp anthranol was suspended in a mixture of water and alcohol and reduced by the aluminium–mercury couple. No tar formed, and when the mixture was stirred into dilute hydrochloric acid the hydroxyanthracene was precipitated, in theoretical yield, as a pale buff solid.

2 : 3-*Diacetoxyanthracene* was prepared by boiling this solid with acetic anhydride and pyridine; after one recrystallisation from rectified spirit, it formed white, elongated, hexagonal plates of constant m. p. 175° [Found : C, 73·4; H, 4·8; CH_3·CO, 29·5; *M*, cryoscopic in naphthalene, 286, 290. $C_{14}H_8O_2(CO{\cdot}CH_3)_2$ requires C, 73·5; H, 4·8; CH_3·CO, 29·3%; *M*, 294].

2 : 3-*Dihydroxyanthracene* was obtained pure by hydrolysing the acetyl derivative with a mixture of acetic and hydrochloric acids. It separated as faintly greenish-yellow plates, which began to sublime at about 260° and melted at 282° (Found : C, 79·9; H, 4·8; *M*, cryoscopic in naphthalene, 212, 204. $C_{14}H_{10}O_2$ requires C, 80·0; H, 4·8%; *M*, 210).

2 : 3-Dihydroxyanthracene dissolves in concentrated sulphuric acid with a bright golden-brown colour, and in aqueous caustic soda and in ammonia to pale green solutions. Its solutions in alcohol and in acetone are very light yellow and show a faint purple fluorescence; addition of ferric chloride to these produces a dark bluish-green colour.

(c) *Oxidation of* 2 : 3-*diacetoxyanthracene*. A boiling solution of 1 g. of 2 : 3-diacetoxyanthracene in 8 c.c. of glacial acetic acid was carefully treated with 1·6 g. of chromic anhydride dissolved in a mixture of 1·5 c.c. of water and 3 c.c. of acetic acid. After

boiling for 10 minutes, the solution was stirred into water. The precipitate, after drying at 100° (1·1 g.), melted at 206—209°, and, after recrystallisation from pyridine, at 211—213°, either alone or when mixed with authentic diacetylhystazarin (Found : C, 66·5; H, 3·7; CH_3·CO, 26·4. Calc. : C, 66·7; H, 3·7; CH_3·CO, 26·6%).

1 : 2-*Thionyldihydroxyanthracene*, $C_6H_4<\begin{matrix}CH\\CH\end{matrix}>C_6H_2<\begin{matrix}O\\O\end{matrix}>SO$.—An excess of cold thionyl chloride reacted very vigorously with 1 : 2-dihydroxyanthracene, but the product did not yield the required thionyl derivative. This was obtained by adding 2·10 c.c. (1 mol.) of freshly-distilled thionyl chloride in 30 c.c. of dry carbon disulphide to a cold solution of 5·85 g. (1 mol.) of 1 : 2-dihydroxyanthracene in a mixture of 4·40 g. (2 mols.) of pyridine and 200 c.c. of dry carbon disulphide. The mixture was boiled on the water-bath for 20 minutes, and the hot disulphide solution was then decanted from the viscous pyridine hydrochloride and concentrated to 50 c.c. The residue in the flask was extracted with a further 200 c.c. of dry carbon disulphide, and this solution also was concentrated. From the two solutions, 4·8 g. of small, pale brown crystals separated. These darkened at about 125° and melted at 138—139° (decomp.) (Found : C, 65·4; H, 3·2; S, 12·6; *M*, cryoscopic in naphthalene, 254, 250. $C_{14}H_8O_3S$ requires C, 65·6; H, 3·1; S, 12·5%; *M*, 256).

1 : 2-*Thionyldihydroxyanthracene* dissolves in cold concentrated sulphuric acid with a transient dark orange colour which rapidly passes to royal-blue; on dilution with water, 2 : 3-dihydroxyanthracene separates. Its solution in cold aqueous caustic soda is light orange-yellow, and when acidified deposits the dihydroxy-compound. The thionyl compound dissolves in cold alcohol to a dark orange solution on which ferric chloride has no apparent effect.

Two finely powdered specimens, after standing in the air for 6 weeks, had their original weights and m. p. and sulphur contents of 12·6 and 12·5%, respectively.

2 : 3-*Thionyldihydroxyanthracene* was obtained in a similar manner to the 1 : 2-compound, 4·50 g. of the dihydroxyanthracene yielding 3·4 g. of the thionyl derivative. This separated from carbon disulphide in thin, faintly yellow flakes, which darkened at 180° and melted at 188° (decomp.) (Found : C, 65·5; H, 3·1; S, 12·6%; *M*, in freezing naphthalene, 260, 264). After standing in air for 6 weeks, a finely-ground specimen had its original weight and m. p. and a sulphur content of 12·6%.

2 : 3-*Thionyldihydroxyanthracene* gives a bright golden-brown solution in cold concentrated sulphuric acid, and a pale yellowish-

green one in cold aqueous caustic soda. These solutions, when respectively diluted with water and acidified, deposit 2 : 3-dihydroxyanthracene. The thionyl compound is very sparingly soluble in hot alcohol, and the very pale yellow solution changes to dark greenish-yellow on addition of ferric chloride.

Action of acetic acid. When 1·1 g. of 2 : 3-thionyldihydroxyanthracene were added to 15 c.c. of boiling glacial acetic acid, very little dissolved and there was no detectable evolution of sulphur dioxide. The addition of two drops of pyridine, however, caused solution to occur with elimination of sulphur dioxide. After boiling for 2 hours, the solution was stirred into cold water; it then deposited 0·9 g. of a dull yellow precipitate, which was filtered off. In order to remove any mechanically-held acetic acid, the moist product was dissolved in hot alcohol, again precipitated with water, filtered off, and thoroughly washed. It was dried over sulphuric acid and examined quantitatively for the acetyl radical, which was absent. A hot acetic acid solution of the remainder of the product, on careful dilution with a warm aqueous solution of sulphur dioxide, deposited 2 : 3-dihydroxyanthracene in pale greenish-yellow plates; these melted at 280—282°, either alone or mixed with the pure compound (Found: C, 79·8; H, 4·9. Calc.: C, 80·0; H, 4·8%).

Action of acetic anhydride. A solution of 0·6 g. of 2 : 3-thionyldihydroxyanthracene in 8 c.c. of boiling acetic anhydride showed no signs of reaction until 1 drop of pyridine was added; sulphur dioxide was then detected. The solution was cooled after 1 hour, and diluted with alcohol; it deposited 0·3 g. of hexagonal plates of 2 : 3-diacetoxyanthracene, which, alone or mixed with an authentic specimen, melted at 175°. The filtrate, when stirred into water, yielded a further 0·4 g. of the same product (Found: $CH_3{\cdot}CO$, 29·5. Calc.: $CH_3{\cdot}CO$, 29·3%).

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THE EDWARD DAVIES LABORATORIES, UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. [*Received, January 29th,* 1927.]

LXXXIV.—*Constitutional Studies in the Monocarboxylic Acids derived from Sugars. Part IV. The Isomeric Lactones obtained from Arabinose.*

By JOHN PRYDE and ROBERT WILLIAM HUMPHREYS.

WITH the view of accumulating more complete information regarding the isomeric forms of the pentose arabinose, we have continued our earlier investigations (Pryde, Hirst, and Humphreys, J., 1925, **127**, 348). Recently, Haworth and Nicholson (J., 1926, 1899) have had occasion to investigate related problems and in as far as our field and theirs have involved common ground we are able fully to corroborate their published findings.

We have now prepared 2 : 3 : 4-trimethyl arabonolactone from two different crystalline derivatives of arabinose, namely, the α- and β-stereoisomerides of trimethyl methylarabinoside. It has been shown by Hirst and Robertson (J., 1925, **127**, 358) that in the presence of acid methyl alcohol these two crystalline derivatives change in optical rotation until a final common equilibrium value of $[\alpha]_D + 150°$ is reached. Such evidence is generally accepted as showing that they are interconvertible α- and β-varieties of the same trimethyl methylarabinoside, possessing one and the same type of oxide linking. It has been clearly established that trimethyl α-methylarabinoside possesses an amylene-oxide linking (Hirst and Robertson, *loc. cit.*), but direct evidence regarding the β-compound is lacking. This evidence we are now able to supply in that it is shown that the crystalline β-compound yields on oxidation a lactone identical in optical rotation and in other physical properties with that obtained from the α-compound. The two stereoisomerides of the parent methylated sugar must therefore possess one and the same type of oxide linking. This is, so far as we are aware, the first *direct* chemical proof that two crystalline stereoisomeric sugars do in fact have a common oxide-linking structure.

The isomeric 2 : 3 : 5-trimethyl arabonolactone has also been prepared from two different sources, namely, by synthesis of the mixed methyl γ-arabinosides and subsequent methylation, followed by simultaneous hydrolysis and oxidation with hydrobromic acid and bromine, and alternatively by bromine oxidation of arabinose followed by methylation. The crystalline lactones obtained by both these processes again proved to be identical with each other, but sharply distinguished in their physical and chemical properties from the liquid 2 : 3 : 4-trimethyl lactone. After the completion of this work, similar results obtained by slightly different methods

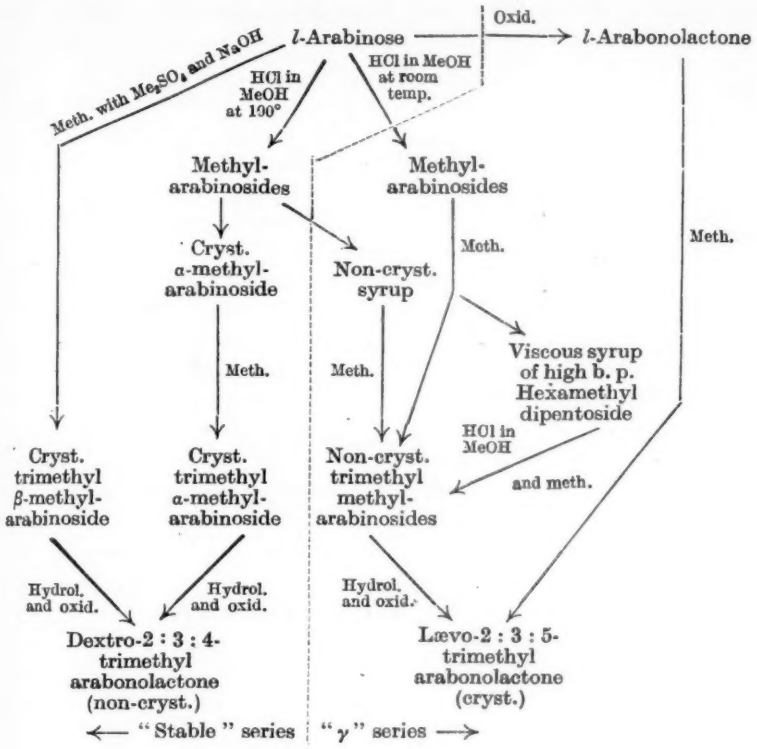
were recorded by Haworth and Nicholson (*loc. cit.*). Particulars of our own preparations are summarised in the following table:

Starting material.	$[\alpha]_D$ in water.	M. p.	Product.	Initial $[\alpha]_D$ in water.	M. p.
Trimethyl α-methyl-*l*-arabinoside.	+250°	44—46°	2 : 3 : 4-Trimethyl arabonolactone.	+176·5°	Liq.
Trimethyl β-methyl-*l*-arabinoside.	+ 26·2	46	„ „	+178·3	Liq.
Trimethyl methyl-*l*-γ-arabinosides.	− 56*	Liq.	2 : 3 : 5-Trimethyl arabonolactone.	− 42·5	29°
l-Arabonolactone.	− 62	Syrup.	„ „	− 43·0	30

* Equilibrium rotation.

The combined results of these four methods of preparing the two isomeric lactones afford clear proof that the stereoisomeric α- and β-derivatives of the normal form of arabinose have a common oxygen linking of the 1 : 5 type, and that a change in the position of this linking to the 1 : 4 type completely alters the nature of the derivatives obtained.

In the course of the foregoing investigations, two further observations of considerable interest were made. Pryde, Hirst, and Humphreys (*loc. cit.*) have already shown that the anomalous rotations obtained in various preparations involving the preliminary condensation of arabinose with methyl alcohol at 100° are to be ascribed to the formation of mixtures of amylene- and butylene-oxidic forms. Evidence has now been obtained which affords a direct proof of this, and of which details will be found in the experimental section of this paper. Levene and Simms (*J. Biol. Chem.*, 1926, **68**, 737) have investigated a similar simultaneous formation of 1 : 5- and 1 : 4-lactone rings in the instance of gluconic acid. The second observation referred to above clearly demonstrated the tendency of γ-arabinose derivatives to enter into an auto-condensation forming a compound apparently of the dipentoside type. The conditions which led to this interesting condensation are being further investigated and publication of the experimental details is deferred until a later date. This brief reference is made here for the purpose of including the observation in the scheme which follows. Of some 11 g. of mixed methyl-γ-arabinosides, which had been prepared by the cold acid methyl alcohol method, it was found that some 6—7 g. had undergone auto-condensation to form a dipentoside, which was eventually reconverted into the simple methylated monopentoside in very good yield.



EXPERIMENTAL.

Preparation of 2 : 3 : 4-*Trimethyl Arabonolactone from Trimethyl* α-*Methylarabinoside.*—This preparation has been described by Pryde, Hirst, and Humphreys (*loc. cit.*). It only remains to add that later preparations of the lactone yielded products with higher initial specific rotations in water, but with identical equilibrium values. Thus, initial values of + 176°, falling to + 21·4° and 21·95° on equilibration in water, and 21·55° from the sodium salt have been obtained (compare the earlier values of + 145°, equilibrating to 22·4° in water, and 22·9° from the sodium salt).

Preparation of 2 : 3 : 4-*Trimethyl Arabonolactone from Trimethyl* β-*Methylarabinoside.*—The crystalline trimethyl β-methylarabinoside was obtained by direct methylation of *l*-arabinose by sodium hydroxide and methyl sulphate as described by Hirst and Robertson (*loc. cit.*). It had an initial $[\alpha]_D$ + 26·17° in methyl alcohol, an equilibrium value, after heating in acid methyl alcohol, of $[\alpha]_D$ + 151·6°, and m. p. 46°. It was converted into the lactone by treatment with hydrobromic acid and bromine by the method

described by Pryde, Hirst, and Humphreys (*loc. cit.*). The lactone was obtained as a colourless, mobile syrup (Found: C, 50·4; H, 7·4; OMe, 47·9. Calc.: C, 50·5; H, 7·4; OMe, 48·9%), which had an initial $[\alpha]_D$ in water ($c = 1·12$) + 178·3°, falling in 24 hours to an equilibrium value $[\alpha]_D$ + 21·5°. The equilibrium value determined from the sodium salt ($c = 0·94$) was + 22·13°. 0·102 G. of lactone required 5·35 c.c. of N/10-alkali (calc., 5·40 c.c.).

Preparation of 2 : 3 : 5-*Trimethyl Arabonolactone from Trimethyl Methyl-γ-arabinosides.*—The trimethyl methyl-γ-arabinosides were obtained as a syrupy mixture by the method of Baker and Haworth (J., 1925, **127**, 365). During the formation of the methyl-γ-arabinosides a minimum specific rotation of − 42·8° was observed some 28 hours after the complete solution of the arabinose in the cold acid methyl alcohol, whilst in a second preparation a minimum value of − 47·14° was recorded. In the latter case, the syrupy product, when isolated, showed $[\alpha]_D$ − 47·55° ($c = 1·152$). Methylation with sodium hydroxide and methyl sulphate followed by Purdie's reagents yielded a syrup with the composition of trimethyl methylarabinoside, which, after distillation in a high vacuum, had $n_D^{15·5°}$ 1·4370 and $[\alpha]_D$ in water − 33·62 ($c = 0·81$), in methyl alcohol − 34·37° ($c = 0·91$), and an equilibrium rotation, after heating for 5 hours in acid methyl alcohol, of $[\alpha]_D$ − 56·33°. These results are all in good accord with those of Baker and Haworth. These authors isolated trimethyl-γ-arabinose by hydrolysis of the fully methylated arabinoside, and oxidised the free sugar to the corresponding monocarboxylic acid by means of nitric acid. In the present communication, simultaneous hydrolysis and oxidation of the arabinoside was achieved by using hydrobromic acid containing bromine. From 17 g. of trimethyl methyl-γ-arabinosides there were obtained, after vacuum distillation, 14 g. of a mobile liquid, b. p. 115°/2 mm., $n_D^{17°}$ 1·4452. This product soon solidified, yielding crystals which had m. p. 29° after being dried on porous tile (Found: C, 50·4; H, 7·3; OMe, 48·5. Calc.: C, 50·5; H, 7·4; OMe, 48·9%). 0·1355 G. of lactone required 7·15 c.c. of N/10-alkali (calc., 7·11 c.c.). $[\alpha]_D$ in water − 42·53°, after 10 days − 34·5° ($c = 1·12$). It is obvious from these figures that the lactone is identical with that obtained by Baker and Haworth by a different method. The lactone did not reduce Fehling's solution even on boiling, but instantly reduced alkaline permanganate in the cold.

Preparation of 2 : 3 : 5-*Trimethyl Arabonolactone from* l-*Arabonolactone.*—A similar preparation has been described by Haworth and Nicholson (*loc. cit.*), but the present work was completed prior to the publication of their results. Their methods differ somewhat

from our own, and the following brief description of the latter is given. 15 G. of *l*-arabinose in 80 c.c. of water were shaken with 30 g. of bromine for 3 hours until solution was complete. The solution was then heated on a water-bath at 40°, and after 20 hours all reducing action had disappeared. The excess of bromine and the hydrobromic acid were removed in the usual manner and finally there were obtained 14·3 g. of arabonic acid as a pale yellow, viscous syrup. Great difficulty was experienced in converting this completely into the lactone, for even after treatment over phosphorus pentoxide at 100°/1 mm. the value of the specific rotation was only — 62°, whereas Fischer and Piloty (*Ber.*, 1891, **24**, 4214) record — 73·9° for their crystalline lactone. We did not obtain the lactone in a crystalline condition, owing either to its content of some 10% of unchanged arabonic acid, or more probably to the fact that it was not allowed sufficient time to crystallise. It was decided to subject the non-crystalline product to methylation.

Methylation of l-*Arabonolactone.*—This was carried out by means of Purdie's reagents, methyl alcohol being used as extraneous solvent in the first two methylations. During the removal of solvent in the recovery of the methylated product after the first methylation, a little methyl oxalate distilled over, showing the presence of a small amount of oxalic acid in our original preparation of the lactone. After a third methylation in the absence of an extraneous solvent, some 12 g. of a pale yellow, mobile syrup were obtained which on distillation gave the following fractions:

Fractions	I	II	III
Weight (g.)	0·5	10	0·5
B. p. at 1 mm.	70°	95—105°	130—140°
$n_D^{14°}$	1·4150	1·4450	1·4462
OMe %	57·4	53·1	45·2

(Calc. for methyl tetramethylarabonate, methyl trimethylarabonate, and trimethyl arabonolactone: OMe, 65·7, 55·8, and 48·9%, respectively.)

Fraction I obviously contained some methyl tetramethylarabonate and hence fractions II and III only were submitted to a fourth methylation and again distilled. The main portion (8 g.) distilled at 100—105°/1 mm. It had $n_D^{15°}$ 1·4396, OMe 55·0%, and $[\alpha]_D$ in water — 8·4° ($c = 1·21$). This product is therefore essentially the methyl ester of trimethylarabonic acid.

Hydrolysis of the Ester and Preparation of 2 : 3 : 5-*Trimethyl Arabonolactone.*—7 G. of the ester were hydrolysed with approximately *N*-barium hydroxide at 85°. The barium was quantitatively precipitated as the sulphate and, the filtrate being worked up in the usual way, 5 g. of a colourless, mobile liquid were collected at 106°/1 mm. This had $n_D^{15°}$ 1·4452 and soon formed a solid mass

of white crystals, m. p. 30°, after drying (Found : C, 50·3; H, 7·4; OMe, 48·3. Calc. : C, 50·5; H, 7·4; OMe, 48·9%). 0·0989 G. of lactone required 5·26 c.c. of *N*-alkali (calc., 5·20 c.c.). It showed an initial $[\alpha]_D$ — 43·05° in water (c = 1·0), changing after 7 days to — 35·5° and after 20 days to — 25·46°. This aqueous solution still behaved essentially as a lactone on titration, showing that only partial conversion into the acid had occurred. The following alterations of specific rotation were observed on acidifying a solution of the sodium salt (c = 1·01); the times recorded are from the moment of adding excess of acid : 2 mins. — 4·1°; 3 mins. — 5·03°; 6 mins. — 7·58°; 60 mins. — 24·29°; 24 hours — 26·23° (t = 18°). The free acid must therefore have a specific rotation of the order — 2°. The same equilibrium mixture of acid and lactone is obtained whether one starts with the lactone or with an acidified solution of the sodium salt.

Direct Proof of the Simultaneous Formation of Amylene- and Butylene-oxidic Forms of Arabinose Derivatives.—From a mixture of methylarabinosides obtained by the initial condensation of *l*-arabinose in acid methyl alcohol at 100°, the α-methylarabinoside was separated in a crystalline form, and this on subsequent methylation and oxidation was found to yield *d*-2 : 3 : 4-trimethyl arabonolactone. The residual mother-liquor from the crystalline α-methylarabinoside was evaporated to a syrup, and the product (10 g.) was methylated twice with sodium hydroxide and methyl sulphate and once by Purdie's reagents. The methylated product was then distilled in a high vacuum, and the main fraction (about 6 g.) distilled at 94°/0·5 mm. It had OMe, 59·0% (calc., 60·2%). As the original syrup separated from the crystalline α-arabinoside was naturally thought to be in large part the corresponding β-derivative, the distilled, fully methylated product was expected to yield crystalline 2 : 3 : 4-trimethyl β-methylarabinoside. No crystallisation could, however, be induced even on nucleating with a crystal of trimethyl β-methylarabinoside. Nucleation with a crystal of the α-stereoisomeride likewise gave a negative result. The product had a specific rotation in water of — 15°, and this lævorotation was assumed to indicate the presence of the γ-, *i.e.*, the butylene-oxidic, form of the sugar. This was fully confirmed on subjecting the liquid to simultaneous hydrolysis and oxidation in the usual manner. There was obtained a final product which, on being cooled and nucleated with a crystal of 2 : 3 : 5-trimethyl arabonolactone, yielded about 4 g. of crystals. These were purified on a tile and were found to be identical in every way with 2 : 3 : 5-trimethyl arabonolactone, having m. p. 29° and $[\alpha]_D$ — 42·4° (c = 1·02). It is thus clear that the original condensation of arabin-

ose with methyl alcohol in the presence of hydrogen chloride at 100° must have resulted in the simultaneous formation of derivatives of the amylene- and butylene-oxidic types. It would also appear that only a relatively small amount of the β-stereoisomeride of the stable (amylene-oxidic) derivative was formed, since none could be separated from the fully methylated arabinoside product, and the final yield of butylene-oxidic lactone, allowing for experimental losses, was not far short of what might be expected had the whole of the non-crystalline syrup consisted of the butylene-oxidic form.

The expenses of this research were defrayed in part by a grant from the Medical Research Council, to whom we wish to express our grateful thanks. We are also indebted to the Department of Scientific and Industrial Research for a maintenance grant to one of us (R. W. H.).

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LXXXV.—*Nature of the Alternating Effect in Carbon Chains. Part XII. Nitration of some Derivatives of Methyl Benzylaminoformate.*

By JOHN WILLIAM BAKER.

IT has recently been shown (Goss, Ingold, and Wilson, J., 1926, 2440) that the acetyl derivatives of benzylamine, methylbenzylamine, and dibenzylamine nitrate mainly in the *op*-positions, it being assumed that the dissociation of the entity $R_3\overset{+x}{N}\!:\!\underset{x}{H}\!:\!\underset{y}{\overset{-y}{O}}\cdot NO_2$ (I) at *xx* becomes important and leads to the formation of a smaller amount of the *m*-isomeride than in the cases of the corresponding unacetylated bases. It was also assumed that the nitrogen atom does not acquire a sufficiently strong or permanent charge by betaine isomerisation for any considerable *m*-substitution to arise from this cause.

In order, if possible, to obtain further information as to the relative effects of these two opposing influences (internal and external ammonium-salt formation), it was considered of interest to determine the behaviour on nitration of the corresponding methyl benzylaminoformates, $C_6H_5\cdot CH_2\cdot NR\cdot CO_2Me$ (II), which are constituted similarly to the acetobenzylamides in so far as concerns the possibility of betaine isomerisation, $R_2\overset{+}{N}\!\!\rangle\!=\!C\!<\!\overset{\overset{-}{O}}{OMe}$,

excepting that, presumably owing to this cause, their basicity appears to be less. The present communication deals with the nitration of methyl benzyl-, dibenzyl-, and benzylmethyl-aminoformates (II; R=H, CH_2Ph, and Me, respectively). These substances are less basic than the corresponding acetyl derivatives; *e.g.*, acetomethylbenzylamide is completely soluble in cold 3% hydrochloric acid, whilst the benzylmethylaminoformate is soluble only in concentrated acid; acetodibenzylamide is easily soluble in concentrated hydrochloric acid, whereas the dibenzylaminoformate is almost insoluble. Hence it would be expected that dissociation of the salt (I) at *yy* (promoting meta-substitution) will be somewhat less, and at *xx* (promoting primarily *op*-substitution) somewhat greater, in the urethanes than in the corresponding acetobenzylamides. On the other hand, the urethanes would probably have a greater tendency towards a betaine phase, so that it is difficult to foretell how the proportions of meta-isomeride formed on nitration should compare with those obtained from the acetyl compounds; they should, however, be of the same order of magnitude, and therefore considerably less than those obtained from the corresponding unsubstituted bases.

Whilst great accuracy cannot be claimed for the figures obtained where only small quantities of the *m*-compound are produced (compare the following paragraph), the actual proportions of meta-isomeride found in the cases considered, $C_6H_5{\cdot}CH_2{\cdot}NR{\cdot}CO_2Me$, are as follows: R = Bz, 14%; R = Me, 12%; R = H, 11%; the corresponding figures for the acetyl derivatives, $C_6H_5{\cdot}CH_2{\cdot}NRAc$, being R = Bz, 25%; R = Me, 8%; R = H, 7%; whilst those of the unsubstituted bases, $C_6H_5{\cdot}CH_2{\cdot}NHR$, are, respectively, 76%, 69%, and 44%.

Unfortunately, the determination of the meta-content of the nitration mixtures by the bromate-titration method (Goss, Ingold, and Wilson, *loc. cit.*) was possible only in the case of the dibenzyl compound (see p. 571), and, moreover, the experimental error in this method is relatively great when only small amounts of the meta-isomeride are present. A method, based on that given by Holleman (*Rec. trav. chim.*, 1899, **18**, 268) and believed to be, when applicable, a definite improvement on the preceding one, was tested in this investigation with a view to its use in future cases in which only very small amounts of meta-isomeride might have to be estimated. In principle, the method depends on the extraction, at a constant temperature, of a known weight of the mixed nitrobenzoic acids, formed on oxidation of the nitration product, with a solution saturated with respect to the *o*- and *p*-isomerides and determination of the increase in acidity due to the dissolved meta-

compound by titration with standard (N/100) baryta solution. Subsequent extraction with a solution saturated with respect to the *o*-, *p*-, and *m*-acids allows a correction to be applied for any small amount of foreign acid matter present. Full details will be found in the experimental portion of this paper, and the results show that the method gives moderately consistent values for the meta-content of the mixtures.

Experimental.

A. *Preparation of Derivatives of Methyl Benzylaminoformate.*

Methyl benzylaminoformate was prepared by the method of Wieman and Jongkees (*Rec. trav. chim.*, 1906, **25**, 243) and had m. p. 62—64° (Found : N, 8·5. Calc. : N, 8·5%).

Methyl Benzylmethylaminoformate.—A solution of methyl chloroformate (2·7 g.) in dry ether was added dropwise with efficient cooling to an ethereal solution of benzylmethylamine (Holmes and Ingold, J., 1925, **127**, 1813) (3·5 g.). A vigorous action took place and the hydrochloride of the base separated. This was decomposed by a slight excess of 10% caustic soda solution, a second molecule (2·7 g.) of methyl chloroformate added, and after a while the whole was acidified with hydrochloric acid and shaken with ether. The residue obtained from the ethereal solution (dried with sodium sulphate) was a colourless, viscous liquid, which was distilled twice under reduced pressure. *Methyl benzylmethylaminoformate* has b. p. 118°/5 mm. (Found : C, 66·3, 66·8; H, 7·5, 7·2; N, 7·5. $C_{10}H_{13}O_2N$ requires C, 67·0; H, 7·3; N, 7·8%).

Great difficulty was experienced in proving the purity of this compound, due, it was subsequently found, to the production of methane during combustion. In order to ensure its purity, benzylmethylamine was fractionated twice under reduced pressure and converted into its hydrochloride by the action of dry hydrogen chloride in dry ether, the hydrochloride was crystallised from absolute alcohol, and the regenerated base again distilled under reduced pressure. This purified specimen and freshly-distilled methyl chloroformate in equimolecular proportion were mixed, with cooling, in dry ethereal solution, the hydrochloride of the base that separated was filtered off, and the methyl benzylmethylaminoformate obtained from the ethereal solution was twice carefully distilled under reduced pressure. The specimen so obtained was a colourless, highly refractive liquid, b. p. 118°/5 mm. On analysis under ordinary conditions, it gave C, 64·6; H, 7·3%, but when mixed with cuprous chloride and slowly burnt in a very hot combustion tube it gave the values recorded above. The gas

obtained in the nitrogen determination (Dumas) contained 43·1% of combustible gas, of which 39·7% was methane, whence the value for the nitrogen content given above was calculated.

Methyl dibenzylaminoformate, obtained in a similar manner from methyl chloroformate and dibenzylamine, had b. p. 199°/13 mm. (Found: C, 75·0; H, 6·7. $C_{16}H_{17}O_2N$ requires C, 75·4; H, 6·7%).

Methyl pp'*-dinitrodibenzylaminoformate* was prepared by the condensation of *pp'*-dinitrodibenzylamine with methyl chloroformate. After crystallisation from ethyl acetate–ligroin it had m. p. 140° (Found: C, 55·8; H, 4·5. $C_{16}H_{15}O_6N_3$ requires C, 55·6; H, 4·4%).

Methyl p*-nitrobenzylaminoformate* was obtained by adding 2·4 g. of methyl chloroformate to molten *p*-nitrobenzylamine (45°), the reaction mixture being diluted with dry ether when it became too solid owing to the separation of the hydrochloride of the base. Isolated as above and crystallised from absolute alcohol, the product had m. p. 109·5° (Found: C, 51·4; H, 4·9. $C_9H_{10}O_4N_2$ requires C, 51·4; H, 4·8%).

B. *Nitration of the Benzylaminoformates and Determination of the Proportion of* m*-Isomeride: General Procedure.*

The conditions of nitration were similar in all three cases studied, the aminoformate being run in (or added in small successive portions if a solid) at the rate of approximately 1 g. per hour to mechanically stirred nitric acid (*d* 1·442: acid of greater density produces a large proportion of dinitrated compounds) at 0°. The isolation of the product varied somewhat from case to case and is described below.

As stated in the introduction, the bromate-titration method gave trustworthy results only for methyl dibenzylaminoformate. In the other cases, the proportion of *m*-isomeride was determined by the solubility method described below.

In each of four 200 c.c. stoppered bottles (*A*, *B*, *C*, and *D*) were placed 80 c.c. of a solution of *o*- and *p*-nitrobenzoic acids saturated at 24°, together with some of the pure solid acids in order to ensure saturation. *A* served as a control. Into *B*, *C*, and *D* were weighed quantities (about 1 g.) of the mixtures of nitrobenzoic acids obtained by oxidation of the nitration products, the weight in each being such that the quantity of *m*-acid was considerably less than that required to saturate the 80 c.c. of water present. The four bottles were fixed in a frame and rotated for 36—48 hours in an electrically controlled thermostat at 24·5° ($\pm$0·5°). They were kept stationary at the same temperature for a further period of 24 hours and the clear supernatant liquors were then filtered, the first few c.c. being

rejected, since a certain error is otherwise introduced owing to slight adsorption on the filter-paper. All the operations, except the final titration, were carried out in the thermostat, and all the apparatus used was stored therein. An aliquot portion (10 c.c.) of each filtrate was withdrawn (in pipettes calibrated relatively to one another) and titrated with $N/100$-baryta and phenolphthalein. The residual untitrated liquors were returned to their respective flasks and to each was added sufficient pure *m*-nitrobenzoic acid to saturate it, and the operations were repeated. The differences between the volumes of baryta required for *B*, *C*, and *D*, respectively, and the volume required for *A* represent the amounts of foreign acid present which must be subtracted from the volume differences found in the first titrations in order to give correct values for the *m*-nitrobenzoic acid present. Holleman (*loc. cit.*) found that the solubility of the *o*- and *p*-acids increased in the presence of an appreciable quantity of the *m*-isomeride, and therefore a correction curve was plotted from the following figures, obtained in preliminary determinations of small, weighed amounts of *m*-isomeride added :

Meta added	14·6	19·5	23·3	39·4	54·0	61·2	87·2	115·1 mg.
Meta found	13·0	15·0	22·2	38·6	52·7	66·6	92·9	133·4 ,,

C. *Details of Individual Cases.*

I. *Methyl Dibenzylaminoformate.—Experiment* 11. The nitration product was poured on crushed ice and made alkaline by the addition of potassium hydroxide solution. The somewhat sticky precipitate produced was filtered off and washed free from gum with a large volume of ether (it dissolved and almost immediately crystallised). The aqueous filtrate was extracted with ether, and the combined extract and washings were worked up in the usual manner, yielding a very viscous gum which slowly solidified (total yield, 94% of the theoretical) [Found for the crystalline solid (30% of the product): C, 55·9; H, 4·6. Found for the gum (70%): C, 55·1; H, 4·4. $C_{16}H_{15}O_6N_3$ requires C, 55·6; H, 4·4%]. The titration of the pure *p*-nitro-isomeride gave a mean bromination number (compare Goss, Ingold, and Wilson, *loc. cit.*) $F = 2{\cdot}175$, whilst for the crystalline solid and the gum were found $F = 2{\cdot}373$ and 2·282, respectively, representing meta-contents of 20% and 11%, respectively. Hence the meta-content of the whole nitration product is (20% of 30%) + (11% of 70%) = 14%.

Experiment 12. The nitration product obtained from 5·0 g. of methyl dibenzylaminoformate was separated into three fractions: (α) a solid, 1·44 g., m. p. 132—135°; (β) a second solid fraction, 2·482 g., m. p. 100—103°, which crystallised from the

ethereal extract; and (γ) a residual gum, 2·374 g. (total yield, 93% of the theoretical) [Found: (α) C, 55·9; H, 4·6; (β) C, 55·9; H, 4·7; (γ) C, 55·8; H, 4·6%]. Each fraction was separately titrated by the bromate method and gave bromination numbers α, 2·195; β, 2·225; γ, 2·435, corresponding to respective meta-contents of 2%, 5%, and 26%, whence the meta-content of the whole nitration product is 13%. Fraction (γ) was oxidised by potassium permanganate to the mixed nitrobenzoic acids (yield, 64%) (Found: *M*, by titration, 165·8. Calc.: *M*, 167), which were separated by the method of Baker and Ingold (J., 1926, 2469). The separated *p*-acid (57%) had m. p. 210—215°; after crystallisation from water it had m. p. 232° (mixed m. p. with pure *p*-acid, 237°). The separated *m*-acid (19%) had m. p. 122°, which was raised to 136° by crystallisation from ethyl acetate–ligroin (mixed with the pure *m*-acid, it melted at 141°). Crystallisation of the fraction α from ethyl acetate–ligroin gave pure methyl *pp'*-dinitrodibenzylaminoformate, which, alone or mixed with a synthetic specimen, melted at 140°.

II. *Methyl Benzylmethylaminoformate.—Experiment* 21. The nitration product was poured on crushed ice, an oil being precipitated, and was made alkaline with potassium hydroxide solution; the whole was then extracted with ether. The gum obtained from the dried ethereal extract failed to crystallise (yield, 92·5% of the theoretical) (Found: C, 54·4; H, 5·8. $C_{10}H_{12}O_4N_2$ requires C, 53·6; H, 5·4%). A further 3% of the material was accounted for as an acid fraction produced by oxidation during the nitration. The neutral nitration product was oxidised with boiling 2% potassium permanganate solution (yield, 77%), and the content of *m*-acid in the mixed nitrobenzoic acids produced (Found: *M*, by titration, 162. Calc.: *M*, 167) was determined by the solubility method: 0·6052 g. required 48·00 c.c. of 0·01029*N*-baryta for the *m*-acid present; this corresponds to 0·08251 g. of *m*-acid, which becomes 0·0735 g. after correction. The content of *m*-acid is therefore 12%.

III. *Methyl Benzylaminoformate.—Experiment* 33. The nitration product, worked up as in the previous case, gave a solid (yield, 81%) (Found: C, 51·1; H, 4·8. $C_9H_{10}O_4N_2$ requires C, 51·4; H, 4·8%) which, after crystallisation from ethyl alcohol, had m. p. 109·5°. This consisted of the pure *p*-nitro-compound, since it gave no m. p. depression in admixture with a synthetic specimen and on oxidation with 2% potassium permanganate solution gave pure *p*-nitrobenzoic acid, m. p. 237° (alone or mixed with a genuine specimen). Determinations of the content of *m*-acid by the bromate method gave bromination numbers of $F = 2·850$, 2·880, 2·850, 2·900. The values of F for the pure *p*- and *m*-isomerides are, how-

ever, 2·870 and 3·050, respectively. The difference is too small for this method to give trustworthy results.

Experiment 34. The nitration product (yield, 83%, a further 6% being accounted for as acid products) (Found: C, 51·2; H, 5·0%) was oxidised with 2% potassium permanganate solution (yield, 86%), and the meta-content of the resulting mixture of nitrobenzoic acids (Found: *M*, by titration, 165·6. Calc.: *M*, 167) determined by the solubility method: 0·8424 g. of the mixed acids required 59·84 c.c. of 0·01029*N*-baryta for the *m*-acid present; this corresponds to 0·1029 g. of *m*-acid, which becomes 0·091 g. after correction. The content of *m*-acid is therefore 11%.

The author wishes to express his gratitude to Professor C. K. Ingold, F.R.S., for his kindly interest and advice during the course of this investigation, and to the Government Grant Committee of the Royal Society for a grant towards the expense.

THE UNIVERSITY, LEEDS. [*Received, November 29th*, 1926.]

LXXXVI.—*Elimination of the Amino-group of Tertiary Amino-alcohols. Part IV. The Displacement of the Amino- by the Hydroxy-group.*

By ALEX. MCKENZIE and ROBERT ROGER.

As was stated in Part I (J., 1923, **123**, 79) of this series of papers, the study of the deamination of tertiary amino-alcohols was initiated from its bearing on the rôle of nitrous acid in the Walden inversion. It was anticipated that the action of nitrous acid on an optically active amino-alcohol, such as *d*-β-hydroxy-αββ-triphenylethylamine, would proceed on the orthodox lines, and by giving either *d*- or *l*-triphenylethylene glycol would provide additional data for the Walden inversion:

$$d\text{-}C_6H_5\cdot CH(NH_2)\cdot CPh_2\cdot OH \longrightarrow d\text{-} \quad \text{or} \quad l\text{-}C_6H_5\cdot CH(OH)\cdot CPh_2\cdot OH.$$

It is, however, impossible to realise this change experimentally, as the product is invariably the optically inactive ketone, phenyldeoxybenzoin (J., 1925, **127**, 283). That this reaction, which involves the migration of a hydrocarbon residue, is a very general one is obvious from the following examples:

$$OH\cdot CPhR\cdot CHR'\cdot NH_2 \longrightarrow R\cdot CO\cdot CHPhR'$$

(R = R′ = Ph: J., 1923, **123**, 79; 1925, **127**, 283.
R = Me; R′ = Ph: J., 1923, **123**, 79; 1924, **125**, 844.

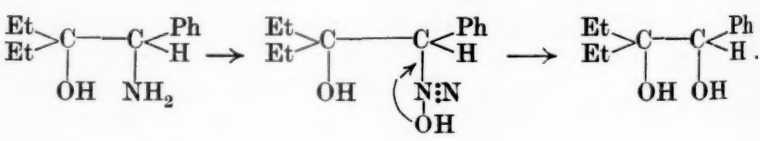
R = $C_{10}H_7$; R′ = Ph: J., 1924, **125**, 2105; Orékhov and Tiffeneau, *Compt. rend.*, 1924, **178**, 1619.
*R = Ph; R′ = Me: J., 1925, **127**, 283.
*R = Ph; R′ = CH_2Ph: J., 1925, **127**, 283.
R = Ph; R′ = H: Bettzieche, *Z. physiol. Chem.*, 1924, **140**, 273; Orékhov and Roger, *Compt. rend.*, 1925, **180**, 70.)

$$OH\cdot CRR'\cdot CHR''\cdot NH_2 \longrightarrow R\cdot CO\cdot CHR'R''$$

(R = Ph; R′ = C_6H_4·OMe; R″ = H: Orékhov and Roger, *loc. cit.*
R = Ph; R′ = $C_{10}H_7$; R″ = H: Luce, *Compt. rend.*, 1925, **180**, 145.
R = R′ = CH_2Ph; R″ = Ph: J., 1926, 779; Bettzieche and Ehrlich, *Z. physiol. Chem.*, 1925, **150**, 197.)

Despite the regularity with which a hydrocarbon residue migrates in those reactions, we thought that it might be possible to select a suitable amino-alcohol in which the normal displacement of the amino- by the hydroxy-group could be effected by the aid of nitrous acid. This has now been accomplished in two instances, in one of which the glycol was the main product, whilst in the other the glycol also was isolated, although the main product was the ketone.

When β-amino-αα-diethyl-β-phenylethyl alcohol, prepared by the method of Thomas and Bettzieche (*Z. physiol. Chem.*, 1924, **140**, 244), was acted on by nitrous acid, the crystals which were isolated consisted of α-phenyl-ββ-diethylethylene glycol, which had previously been prepared by Tiffeneau and Lévy from magnesium ethyl bromide and ethyl *dl*-mandelate (*Bull. Soc. chim.*, 1923, **33**, 735). The mechanism of the action may be outlined as follows:

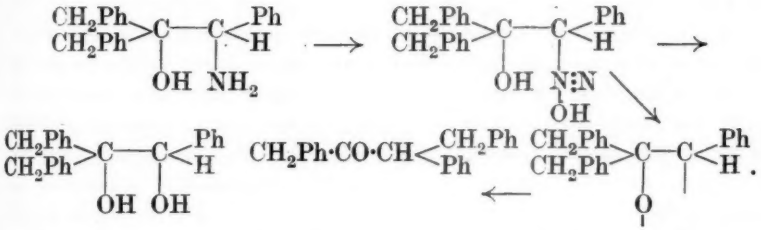


As in semipinacolinic deamination, the formation of an intermediate unstable diazo-compound is assumed, but water is not produced, the hydroxy-group migrating from nitrogen to carbon. No transposition of the ethyl group was detected.

The main product of the deamination of β-amino-β-phenyl-αα-dibenzylethyl alcohol, prepared by the action of magnesium benzyl chloride on ethyl *r*-phenylaminoacetate hydrochloride, is

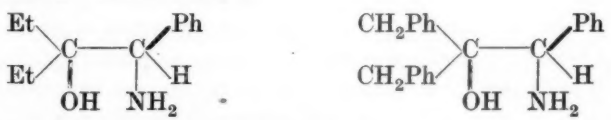
* The preparation of optically active ketones from *d*-alanine, *d*-phenylalanine and *l*-phenylalanine has also been described (J., 1926, 779).

benzyl αβ-diphenylethyl ketone (J., 1926, 779), but the mother-liquors from which this ketone had been crystallised gradually deposited crystals from which α-phenyl-ββ-dibenzylethylene glycol, m. p. 115—116°, has now been isolated. The identity of this glycol was established by comparison with the compound prepared from magnesium benzyl chloride and ethyl *dl*-mandelate (Orékhov, *Bull. Soc. chim.*, 1919, **25**, 111). Here, semipinacolinic deamination was accompanied by the ultimate displacement of the amino- by the hydroxy-group :



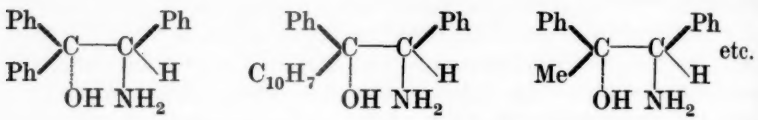
From several viewpoints, this normal action of nitrous acid which led to the formation of the two glycols presents points of interest. Thus, it renders the possibility open for the conversion, for example, of *l*-phenylaminoacetic acid into the configuratively-related diethylamino-alcohol, and the transformation of the latter into a glycol which could then be contrasted with that obtainable by the action of magnesium ethyl bromide on ethyl *l*-mandelate.

It will also be observed in those cases where nitrous acid behaved normally that the two hydrocarbon residues attached in the amino-alcohol to the carbon atom to which the hydroxy-group is also bound are groups with a small saturation capacity. Ample evidence of the low saturation capacity of both the ethyl and the benzyl group is provided by the important researches of Tiffeneau, Orékhov, and Mlle. Lévy. In the two amino-alcohols under discussion, the hydroxy-group is in each case firmly linked to the carbon atom, and semipinacolinic deamination would accordingly be retarded, if not entirely prevented. On this conception, the amino-alcohols could be depicted as follows :



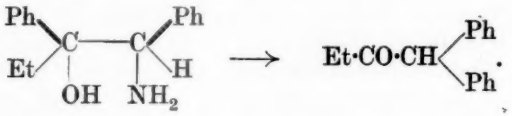
On the other hand, the striking fact emerges that in every instance of semipinacolinic deamination studied by us (with the exception of that of β-amino-β-phenyl-αα-dibenzylethyl alcohol), the strong saturation capacities of the hydrocarbon residues have caused

the tertiary hydroxy-group to be comparatively loosely bound, thus:



When such compounds are acted on by nitrous acid, the hydroxy-group should readily combine with hydrogen with the elimination of water, and it actually does this.

It will also be noticed that in the examples quoted both of the hydrocarbon residues associated with the tertiary hydroxy-group have either weak or strong saturation capacities. An example is now described where one of the residues has a strong and the other a weak saturation capacity. A compound possessing this type of grouping was prepared by the action of magnesium ethyl iodide on desylamine hydrochloride, and it was found to undergo semi-pinacolinic change with nitrous acid:



The phenyl group migrated, the sole product isolated being diphenylbutanone. Now, the corresponding glycol, ethylhydrobenzoin, has been dehydrated by Tiffeneau and Orékhov (*Bull. Soc. chim.*, 1921, **29**, 422), who found that, under the influence of concentrated sulphuric acid, this glycol was transformed into a mixture of diphenylbutanone and ethyldeoxybenzoin. Our present experiments show that phenyl has a greater migrational aptitude than ethyl. Further, there was no evidence of the formation of ethylhydrobenzoin, and the hydroxy-group of the amino-alcohol was, therefore, less firmly bound than in the diethyl- or dibenzyl-amino-alcohols.

It should be emphasised that in addition to the effect of the ethyl and benzyl groups in causing the tertiary hydroxy-group to be firmly bound in β-amino-αα-diethyl-β-phenylethyl alcohol and in β-amino-β-phenyl-αα-dibenzylethyl alcohol, the phenyl group, which is attached to the same carbon atom as is the amino-group, would probably also be a contributory factor, although to a less degree than the ethyl and benzyl groups. The peculiar influence of the phenyl group has already been referred to by Mlle. Lévy in other connexions (*Bull. Soc. chim.*, 1923, **33**, 1655; 1926, **39**, 67).

It is also noteworthy that the best yield of glycol was obtained

from that amino-alcohol in which the hydrocarbon residues attached to the tertiary carbon atom were purely aliphatic.

EXPERIMENTAL.

Deamination of β-Amino-αα-diethyl-β-phenylethyl Alcohol.—*r*-Phenylaminoacetic acid was converted into the hydrochloride (1 mol.) of its ethyl ester, which was then acted on by magnesium ethyl bromide (10 mols.). The resulting amino-alcohol (2 g.) was dissolved in 50% acetic acid, and an aqueous solution of sodium nitrite (2·2 g.) was gradually added, the temperature being maintained at 0°. Over-night, the oil had partly solidified; the product was extracted with ether, the extract washed with sodium bicarbonate, and the ether dried and expelled. The solid (1·6 g.) was crystallised thrice from light petroleum (b. p. 60—80°), from which it separated in needles containing no nitrogen, and melting at 89—89·5° (Found: C, 74·0; H, 9·4. Calc. for $C_{12}H_{18}O_2$: C, 74·2; H, 9·3%). The product gave an orange coloration with concentrated sulphuric acid, and was α-phenyl-ββ-diethylethylene glycol, which has m. p. 89° according to Tiffeneau and Lévy (*loc. cit.*).

The mother-liquors yielded a small quantity of oil which may have contained some ketone from semipinacolinic deamination, although no semicarbazone was actually obtained from it.

To eliminate the possibility of the acetic acid having caused the elimination of the amino-group by hydrolysis, a control experiment on the above lines was carried out in which the addition of the sodium nitrite was omitted. No glycol was isolated.

Deamination of β-Amino-β-phenyl-αα-dibenzylethyl Alcohol.—The amino-alcohol was prepared by the action of magnesium benzyl chloride on ethyl phenylaminoacetate hydrochloride. An aqueous solution of sodium nitrite (2·3 g.) was gradually added to the solution of the amino-alcohol (3 g.) in glacial acetic acid (30 g.), the solution being kept at 0° and stirred vigorously. The viscous product did not solidify entirely when kept over-night, and, after the addition of water, it was extracted with ether, the ether extract washed with sodium carbonate, and dried with sodium sulphate. The resulting oil was dissolved by heating with light petroleum (b. p. 60—80°). After the crystals (A) which gradually separated had been removed, the filtrate was evaporated to dryness, and the oil dissolved in ethyl alcohol; crystals (B) which separated were united with (A) and crystallised from ethyl alcohol; 0·6 g. of benzyl αβ-diphenylethyl ketone (m. p. 74—74·5°) was then obtained. The ethyl-alcoholic solution from which (B) had been withdrawn gradually deposited a higher-melting solid, which after crystallisation from rectified spirit gave α-phenyl-ββ-dibenzylethylene glycol, m. p.

115—116°. Yield, 0·5 g. For comparison, the glycol was prepared by the action of magnesium benzyl chloride on ethyl *dl*-mandelate, and there was no depression of the melting point when samples from both sources were mixed.

In another experiment, conducted under somewhat similar conditions with dilute acetic acid (15%, 180 c.c.), 5 g. of the amino-alcohol were acted on by a solution of 4 g. of sodium nitrite. The yield of pure glycol was in this case 1·1 g.

Deamination of β-Amino-α-ethyl-αβ-diphenylethyl Alcohol.—Ten g. of desylamine hydrochloride (1 mol.), prepared by the reduction of benzil β-monoxime with stannous chloride according to Pschorr and Brüggemann (*Ber.*, 1902, **35**, 2740), were added in instalments within 2 hours to the Grignard reagent prepared from 57 g. of ethyl iodide (9 mols.). The temperature was maintained at about 0° during the addition. Over-night, the mixture was boiled gently for 2½ hours, and then decomposed by ice and dilute hydrochloric acid. The acid layer was separated and made alkaline with ammonia; the free amino-alcohol then separated as an oil. The latter was triturated with ice-cold concentrated hydrochloric acid, and the solid hydrochloride (11 g.) was collected and crystallised from dilute hydrochloric acid–ethyl alcohol.

β-Amino-α-ethyl-αβ-diphenylethyl alcohol hydrochloride, $NH_2 \cdot CHPh \cdot CEtPh \cdot OH,HCl$, crystallises in rosettes of feathery needles, m. p. 224—226° (Found: Cl, 12·6. $C_{16}H_{19}ON,HCl$ requires Cl, 12·8%). It gives a transient pink coloration with concentrated sulphuric acid.

A solution of sodium nitrite (2 g.) was gradually added to a solution of the hydrochloride (2·2 g.) in dilute hydrochloric acid, and the resulting oil was extracted with ether. Yield: 2 g. This was acted on by semicarbazide hydrochloride and sodium acetate; 1·3 g. of the solid semicarbazone were then obtained. After crystallisation from rectified spirit, rectangular needles of the semicarbazone of diphenylbutanone separated. These melted at 195—196°, and there was no depression of the melting point on admixture with the semicarbazone of diphenylbutanone prepared by the dehydration of ethylhydrobenzoin with concentrated sulphuric acid.

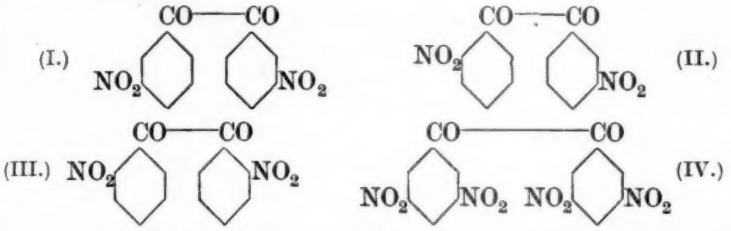
We are indebted to Miss A. W. Cochrane, Miss M. S. Lesslie, and Mr. A. K. Mills for assistance in the preparative work. We also thank the Carnegie Trust for the award of a Fellowship to one of us.

UNIVERSITY COLLEGE, DUNDEE.
UNIVERSITY OF ST. ANDREWS. [*Received, August 3rd*, 1926.]

LXXXVII.—*The Nitration of Benzil.* 3 : 5 : 3′ : 5′-*Tetranitrobenzil.*

By FREDERICK DANIEL CHATTAWAY and EDWARD AUTY COULSON.

IT has recently been shown (Chattaway and Coulson, J., 1926, 1070) that when benzil is nitrated, a mixture of three isomeric dinitrobenzils is obtained, whether the nitration is effected by fuming nitric acid or by a mixture of potassium nitrate and sulphuric acid. The crude product, although consisting largely of 3 : 3′-dinitrobenzil (I), contains considerable amounts of the 2 : 3′- (II) and 2 : 2′-dinitrobenzil (III).



Barnett and Kay, who regarded this crude mixture as pure 3 : 3′-dinitrobenzil, were unable to nitrate it further (*Chem. News*, 1922, **125**, 57), whilst Christie and Kenner (J., 1926, 470) found no difficulty in doing this, and obtained a tetranitro-derivative (m. p. 168°) which must have been a mixture of isomerides.

3 : 3′-Dinitrobenzil having been isolated in a pure state, the further action of nitric acid upon it has been studied.

On nitration by a mixture of fuming nitric acid and sulphuric acid it yields 3 : 5 : 3′ : 5′-*tetranitrobenzil* (IV), m. p. 179°.

The only other substance produced in any recognisable quantity in the nitration is 3 : 5-dinitrobenzoic acid, which is formed in considerable amount as a by-product. That the entering nitro-groups take up the vacant *meta*-positions is shown by the production of an approximately theoretical amount of 3 : 5-dinitrobenzoic acid when the tetranitrobenzil is oxidised by chromic acid.

EXPERIMENTAL.

Isolation of 3 : 3′-*Dinitrobenzil* (I).—3 : 3′-Dinitrobenzil is most readily isolated from the product of the direct nitration of benzil (which melts at about 109°) by cooling rapidly a saturated acetone solution. A pulpy mass of crystals, melting not very sharply near 122°, separates, and a further crop of the 3 : 3′-isomeride, somewhat less pure, is obtained by distilling off part of the acetone from the mother-liquor. The process can be repeated several times

until the 2 : 3′- and 2 : 2′-isomerides are seen among the crystals separating.

The various crops of crystals are then mixed and the process is repeated five or six times, until the melting point has been raised to about 129°. The final purification is best effected by recrystallising the material from acetic acid until the crystals melt sharply at 132°.

3 : 3′-*Dinitrobenzil monophenylhydrazone*,

$$NO_2 \cdot C_6H_4 \cdot C(N \cdot NHPh) \cdot CO \cdot C_6H_4 \cdot NO_2,$$

separates as a pulpy mass of yellow crystals when an alcoholic solution of 3 : 3′-dinitrobenzil (1 mol.) and phenylhydrazine (1 mol.) is boiled for about an hour. It crystallises from boiling acetic acid, in which it is easily soluble, in very slender, yellow prisms, m. p. 171° (Found : N, 14·7. $C_{20}H_{14}O_5N_4$ requires N, 14·4%).

3 : 3′-*Dinitrobenzil osazone*,

$$NO_2 \cdot C_6H_4 \cdot C(N \cdot NHPh) \cdot C(N \cdot NHPh) \cdot C_6H_4 \cdot NO_2,$$

although formed only in very small amount when an alcoholic or acetic acid solution of 3 : 3′-dinitrobenzil or its monophenylhydrazone is boiled with a great excess of phenylhydrazine, separates in considerable amount when phosphorus pentoxide is added to the reaction mixture.

1·5 G. of 3 : 3′-dinitrobenzil (1 mol.) was boiled with 1·5 g. of phenylhydrazine (3 mols.) and 2 g. of phosphorus pentoxide in acetic acid for an hour. On cooling, the osazone separated free from the monohydrazone. It crystallises from boiling acetic acid, in which it is only slightly soluble, in long, slender, bright yellow prisms, which, after drying on the water-bath, contain 1 mol. of acetic acid. This is lost when the compound is heated to 130—140°, the crystals becoming opaque and lighter in colour (Found : loss after heating at 140°, 10·9. $C_{26}H_{20}O_4N_6,CH_3 \cdot CO_2H$ requires loss, 11·1%). The osazone melts at 269° (Found : N, 17·2. $C_{26}H_{20}O_4N_6$ requires N, 17·5%).

2 : 3-*Di*(3′-*nitrophenyl*)*quinoxaline* separates when a solution of equivalent amounts of *o*-phenylenediamine and 3 : 3′-dinitrobenzil in acetic acid is heated. It dissolves sparingly in boiling acetic acid and separates in very pale yellow, rhombic plates, m. p. 213° (Found : N, 15·0. $C_{20}H_{12}O_4N_4$ requires N, 15·1%).

3 : 5 : 3′ : 5′-*Tetranitrobenzil* (IV).—3 : 3′-Dinitrobenzil is so easily nitrated that the action, unless carefully controlled, may become very violent.

A solution of 10 g. of 3 : 3′-dinitrobenzil in 72 g. of concentrated sulphuric acid was heated to 100° and 60 g. of nitric acid (*d* 1·5) were slowly added, the temperature being kept between 100° and 110°. The mixture was then heated on a water-bath for a few hours, cooled, and poured over crushed ice. The yellow, viscid

mass that separated was boiled repeatedly with water to extract the considerable amount of 3 : 5-dinitrobenzoic acid which it contained. The brittle, yellow, crystalline mass melting at about 174° thus obtained was practically pure 3 : 5 : 3′ : 5′-*tetranitrobenzil*, the amount being about one-third of the weight of 3 : 3′-dinitrobenzil used. The aqueous extracts on condensation yielded 3 : 5-dinitrobenzoic acid, m. p. 205°, identical with the dinitrobenzoic acid obtained by nitrating *m*-nitrobenzoic acid (*Z. Chem.*, 1870, 641) and giving no depression of melting point when mixed with it.

3 : 5 : 3′ : 5′-Tetranitrobenzil is sparingly soluble in boiling alcohol and benzene, moderately easily soluble in boiling acetic acid, and separates from these solvents in bright yellow, six-sided, rhombic prisms, m. p. 179° (Found : C, 42·8; H, 1·7; N, 14·4. $C_{14}H_6O_{10}N_4$ requires C, 43·1; H, 1·5; N, 14·4%).

Oxidation of 3 : 5 : 3′ : 5′-*Tetranitrobenzil*.—A solution of 1 g. of 3 : 5 : 3′ : 5′-tetranitrobenzil in 50 c.c. of boiling acetic acid was gradually treated with 0·5 g. of chromium trioxide and boiled gently for a few minutes ; the excess of chromic acid was then reduced with alcohol, and the whole evaporated to small bulk. Addition of hot dilute caustic soda solution in slight excess, filtration, and acidification of the filtrate gave 0·85 g. of 3 : 5-dinitrobenzoic acid, m. p. 205° ; a further 0·12 g. was obtained from the mother-liquor (total yield, 87% of the theoretical).

3 : 5 : 3′ : 5′-*Tetranitrobenzil monophenylhydrazone*,

$$C_6H_3(NO_2)_2\cdot C(:N\cdot NHPh)\cdot CO\cdot C_6H_3(NO_2)_2,$$

is produced when equivalent amounts of the tetranitrobenzil and phenylhydrazine are heated together in alcohol. It is very sparingly soluble in boiling alcohol and benzene, but more soluble in boiling acetic acid, from which it separates in small, yellow, rhombic crystals, m. p. 236° (Found : N, 17·4. $C_{20}H_{12}O_9N_6$ requires N, 17·5%).

Boiling the tetranitrobenzil for a long time with an excess of phenylhydrazine, either alone or in alcohol or acetic acid, or in acetic acid with phosphorus pentoxide, does not produce an osazone.

2 : 3-*Di*(3′ : 5′-*dinitrophenyl*)*quinoxaline* separates when equivalent amounts of *o*-phenylenediamine and 3 : 5 : 3′ : 5′-tetranitrobenzil are heated together in acetic acid solution. It is slightly soluble in boiling acetic acid and separates in short, irregular, colourless prisms which contain 1 mol. of acetic acid. This is lost by drying on the water-bath (Found : loss at 110°, 11·3. Calc. : loss, 11·5%), and the crystals become opaque and melt at 285° (Found : N, 18·5. $C_{20}H_{10}O_8N_6$ requires N, 18·2%).

THE QUEEN'S COLLEGE, OXFORD. [*Received, December 29th*, 1926.]

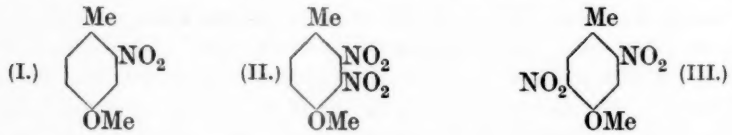
LXXXVIII.—*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. Part IX.* 2 : 3- *and* 2 : 5-*Dinitro*-4-*methoxytoluenes.*

By HERBERT ERIC DADSWELL and JAMES KENNER.

IN an earlier paper (Kenner, Tod, and Witham, J., 1925, **127**, 2343), the behaviour of 4-chloro-2 : 3- and -2 : 5-dinitrotoluenes towards ammonia and sodium methoxide was examined, with the object of comparing the influences of the methyl group and the chlorine atom on the reactivities of the nitro-groups.

A similar comparison of the methyl and methoxyl groups has now been made by a study of 2 : 3- (II) and 2 : 5- (III) dinitro-4-methoxytoluenes.

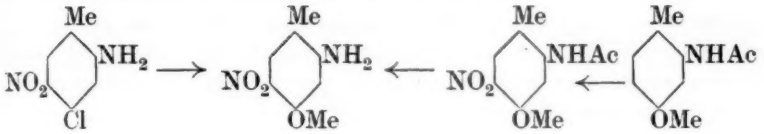
It was stated by Kaufler and Wenzel (*Ber.*, 1901, **34**, 2238) that the former of these compounds is the main product of the nitration of 2-nitro-4-methoxytoluene (I), but a repetition of their work,



whilst confirming the formation of this compound, showed that they had not obtained it in a pure condition, and that the 2 : 5-isomeride also can be isolated from the products of the reaction. The separation is, however, tedious and wasteful, and the ethers are more accessible from 2 : 3- and 2 : 5-*dinitro*-p-*cresols*. These are produced approximately in the proportion of 2 : 1 when 2-nitro-*p*-cresol is nitrated, and are comparatively easily separated. These results are of interest as illustrating the general tendency, emphasised by Jones and Robinson (J., 1917, **111**, 907; compare Rây and Robinson, J., 1925, **127**, 1608), for the entering group in such cases to take up the 3-position, ortho- to the nitro-group. As in the cases of the dimethyl ether of 2-nitroquinol and of 2-nitroaceto-*p*-toluidide (Page and Heasman, J., 1923, **123**, 3240; Scott and Robinson, J., 1922, **121**, 844), however, this does not occur to the entire exclusion of substitution in the 5-position. Conversely, we have found that the conditions prescribed by Scott and Robinson (*loc. cit.*) for the preparation of 2 : 5-dinitroaceto-*p*-toluidide also lead to the production of some of the 2 : 3-isomeride.

A study of the action of methyl-alcoholic ammonia on 2 : 5-dinitro-4-methoxytoluene led to no result useful for the present purpose, for most of the material was recovered unchanged after

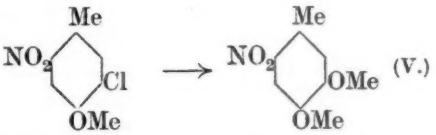
treatment at 140°, and at 150° it was converted into a mixture consisting partly of black insoluble material, from which neither of the expected toluidines could be obtained. Of these, *5-nitro-4-methoxy-o-toluidine* (IV) was obtained by the action of sodium methoxide on 4-chloro-5-nitro-*o*-toluidine (Kenner, Tod, and Witham, *loc. cit.*), and its acetyl derivative was the sole product isolated from the nitration of 4-methoxyaceto-*o*-toluidide :



(IV.)

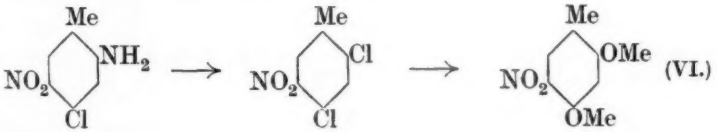
Similarly, 4-methoxyaceto-*m*-toluidide was converted by each of the methods of nitration employed solely into 6-nitro-4-methoxyaceto-*m*-toluidide (compare Limpach, *Ber.*, 1899, **22**, 790). These results are in interesting contrast to the behaviour of the corresponding chloro-compounds, from each of which both the possible isomerides are obtained (Kenner, Tod, and Witham, *loc. cit.*).

Of the possible products of the action of sodium methoxide on the above dinitro-compound, 6-nitrohomoveratrole (V) was already known (Cousin, *Ann. Chim. Phys.*, 1898, **13**, 480; Kostanecki and Paul, *Ber.*, 1902, **35**, 2608; Gilbody and W. H. Perkin, J., 1902, **81**, 1040), and has now been prepared from *3-chloro-6-nitro-4-methoxytoluene* (de Vries, *Rec. trav. chim.*, 1909, **28**, 401) through the agency of sodium methoxide :



(V.)

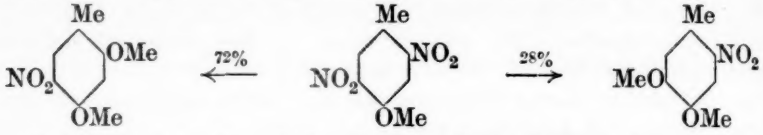
In the same way, *5-nitro-2 : 4-dimethoxytoluene* (VI) resulted from *2 : 4-dichloro-5-nitrotoluene*, derived from 4-chloro-5-nitro-*o*-toluidine (Kenner, Tod, and Witham, *loc. cit.*) :



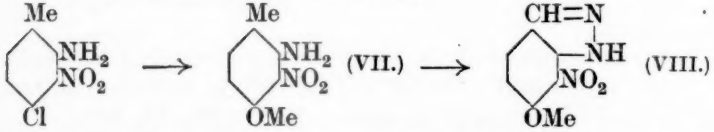
(VI.)

The 2 : 4-dimethoxy-derivative (VI) was also isolated from the mixture of methoxy-derivatives obtained by the action of sodium methoxide on 2 : 5-dinitro-4-methoxytoluene. This indication that displacement of the 2- predominates over that of the 5-nitro-group

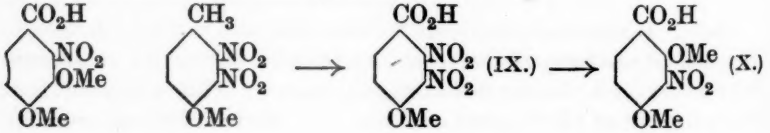
in this reaction was confirmed by thermal analysis, which showed that the two products are formed in the ratio 72 : 28.



Preliminary to the study of the action of ammonia on 2 : 3-dinitro-4-methoxytoluene, 3-*nitro*-4-*methoxy*-o-*toluidine* (VII) was prepared from 4-chloro-3-nitro-*o*-toluidine by treatment with sodium methoxide, and shown to be convertible in excellent yield into 7-nitro-6-methoxyindazole (VIII):



Application of this reaction to the oily mixture of bases obtained from the dinitro-compound indicated that it consisted to the extent of 30% of the *o*-toluidine. In general confirmation of this result, it was possible to isolate from the mixture a base, different from the *o*-toluidine but isomeric with it, which was therefore 2-*nitro*-4-*methoxy*-m-*toluidine*. Attempts were made by a variety of methods to prepare this base from 4-methoxy-*m*-toluidine, but without success. Both it and its isomeride could obviously be converted into the corresponding nitrodimethoxytoluenes—a point of importance in view of the interest recently evinced in the preparation of 2-nitrohomoveratrole (Merck, D.R.-P. 415315; Oberlin, *Arch. Pharm.*, 1925, **263**, 641; Gulland and Robinson, J., 1926, 1976). This was, however, deemed to be unnecessary for the present investigation, since the mixture of dimethoxynitrotoluenes arising from the action of sodium methoxide on 2 : 3-dinitro-4-methoxytoluene was an oil which offered no prospect of being separable into its components by fractional distillation. But its composition followed from its oxidation to a mixture of nitrodimethoxybenzoic acids, in which 2-nitroveratric acid (Pschorr and Sumuleanu, *Ber.*, 1899, **32**, 3409) predominated. The isomeric 3-*nitro*-2 : 4-*dimethoxybenzoic acid* (X) resulted from the action of sodium methoxide on 2 : 3-*dinitro*-4-*methoxybenzoic acid* (IX), which in turn was prepared from 2 : 3-dinitro-4-methoxytoluene.



It thus appears that both ammonia and sodium methoxide displace the 3- rather than the 2-nitro-group of 2 : 3-dinitro-4-methoxytoluene, but that the 2-position of the 2 : 5-isomeride is the more liable to attack. No discrepancy of this kind was observed between the chlorodinitrotoluenes, and it will therefore be of interest to examine the behaviour of 4 : 5-dinitro-2-methoxytoluene.

EXPERIMENTAL.

Nitration of 2-Nitro-4-methoxytoluene.—The quality of the fuming nitric acid available rendered it necessary slightly to modify the conditions used by Kaufler and Wenzel (*loc. cit.*).

Sulphuric acid (60 c.c.) was gradually added to a solution of 2-nitro-4-methoxytoluene (10 g.) in glacial acetic acid (100 c.c.) and nitric acid (*d* 1·49; 40 c.c.) below 5°. The product (12 g.), after prolonged and careful fractional crystallisation from methyl alcohol, yielded 4 g. of material, m. p. 132—133° (Found: N,* 13·2%) as compared with 126—128° recorded by Kaufler and Wenzel for 2 : 3-dinitro-4-methoxytoluene. The identity of the product was proved by its reduction to the diamine, m. p. 75—76° (Kaufler and Wenzel give 72—73°), which was further characterised by condensation with benzil. *8-Methoxy-2 : 3-diphenyl-5-methylquinoxaline* separates from acetic acid in fine, grey needles, m. p. 196—197° (Found: N, 9·15. $C_{22}H_{18}N_2$ requires N, 9·0%).

2 : 5-Dinitro-4-methoxytoluene (0·5 g.) was isolated from the mother-liquors of the above crystallisation and crystallised from benzene–light petroleum in yellow needles, m. p. 123—124° (Found: N, 13·4. Calc.: N, 13·2%). The compound had been previously prepared by G. M. Robinson (J., 1916, **109**, 1089), who found it to melt at 126°. Its orientation was proved by its reduction to a diamine, m. p. 164°, and direct comparison of this with authentic 3 : 6-diamino-4-methoxytoluene from 6-nitro-4-methoxy-*m*-toluidine (Limpach, *Ber.*, 1889, **22**, 791). Further, when a suspension of this base (5·75 g.) in crushed ice (187 g.) was oxidised by shaking it for 20 hours with the paste prepared from potassium persulphate (25 g.) and sulphuric acid (50 g.), the crude nitroso-compound obtained (4·2 g.) furnished 2 : 5-dinitro-4-methoxytoluene (2 g.), m. p. 123—124°, on oxidation at 40—50° with nitric acid (*d* 1·48; 15 c.c.).

Nitration of 2-Nitro-p-cresol.—When a mixture of glacial acetic acid (20 c.c.) and nitric acid (*d* 1·49; 16 c.c.) was added to a solution of 2-nitro-*p*-cresol (40 g.) in glacial acetic acid (160 c.c.) at 18—25°, crystalline material (18 g., m. p. 154—156°) gradually separated. The material (25 g.) precipitated on dilution of the liquor yielded

* Determinations marked with an asterisk were carried out by Pregl's micro-Dumas procedure.

another product (8 g., m. p. 112—113°) by crystallisation from alcohol, 13 g. of material being recovered from the solution. By crystallisation from glacial acetic acid, this furnished 6 g., m. p. 156—157°.

The less fusible product was 2:3-*dinitro*-p-*cresol*, which crystallised from glacial acetic acid in light yellow plates, m. p. 157—158° (Found: N, 14·1. $C_7H_6O_5N_2$ requires N, 14·1%), and was converted, by treatment in alkaline solution at 40—50° with methyl sulphate, into 2:3-dinitro-4-methoxytoluene, m. p. 132—133°. The lower-melting product, light brown needles, m. p. 112—113°, was 2:5-*dinitro*-p-*cresol* (Found: N, 14·2. $C_7H_6O_5N_2$ requires N, 14·1%), since it furnished 2:5-dinitro-4-methoxytoluene, m. p. 123—124°, on alkylation with methyl sulphate.

The possibility of utilising 2:5-dinitro-*p*-toluidine as a source of the cresol was also examined, but abandoned when it was found that the material prepared according to the directions of Scott and Robinson (*loc. cit.*) was a mixture. From 4 g. of the crude base, 1 g. of almost pure 2:5-dinitro-*p*-toluidine, m. p. 186—187°, was obtained by crystallisation first from alcohol and then from benzene. By crystallising the material recovered from the mother-liquors twice from methyl alcohol, 2:3-dinitro-*p*-toluidine (0·75 g.), m. p. 122—123°, was obtained; it was identified by comparison with an authentic specimen. The remaining material was a mixture of the isomerides.

5-*Nitro*-4-*methoxy*-o-*toluidine* was obtained in quantitative yield when 4-chloro-5-nitro-*o*-toluidine (2·7 g.) was heated for 6 hours at 130° with a solution of sodium (0·3 g.) in methyl alcohol (12 c.c.). It separated from methyl alcohol in light purple prisms, m. p. 158—159°, which darkened rapidly on exposure (Found: N, 15·6. $C_8H_{10}O_3N_2$ requires N, 15·4%). It was converted by reduction into the *p*-diamine, m. p. 163°, already mentioned, and furnished an *acetyl* derivative which separated from alcohol in needles, m. p. 154—155° (Found: N, 12·8. $C_{10}H_{12}O_4N_2$ requires N, 12·5%). This compound was also produced apparently as sole product when a solution of 4-methoxyaceto-*o*-toluidide (10 g.) in glacial acetic acid (15 c.c.) and sulphuric acid (20 c.c.) was treated at 15—20° with nitric acid (*d* 1·49; 3 c.c.). It was conveniently hydrolysed in 1 hour by boiling it with 50% sulphuric acid. Attempts to obtain an indazole derivative from the base (compare 3-nitro-4-methoxy-*o*-toluidine, later) were unsuccessful.

6-Nitro-4-methoxyaceto-*m*-toluidide was prepared by Limpach (*loc. cit.*) from 4-methoxyaceto-*m*-toluidide. The nitration was repeated under various conditions which, in the case of acetanilide, are known to favour ortho-nitration: (1) a suspension of the

acetotoluidide (21·6 g.) in acetic anhydride (20 c.c.) was treated at 10—20° with a mixture of nitric acid (*d* 1·48; 10 g.), urea (0·2 g.), and acetic anhydride (6 g.); (2) nitric acid (*d* 1·48; 3 c.c.) was added to a solution of the acetotoluidide (11 g.) in glacial acetic acid (15 c.c.) and sulphuric acid (20 c.c.) at 10—15°; (3) a solution of 4-methoxy-*m*-toluidine (5·5 g.) in acetic anhydride (6 c.c.) was added at 40—50° to a mixture of cupric nitrate (5 g.) and acetic anhydride (15 c.c.) (compare Menke, *Rec. trav. chim.*, 1925, **44**, 141). In every case a large proportion of the pure acetyl derivative was at once obtained, whilst hydrolysis of material recovered from the crystallisation liquors furnished the corresponding amine, with no evidence of its isomeride.

4-*Methoxy*-m-*oxalotoluidide*, from 4-methoxy-*m*-toluidine and ethyl oxalate, was precipitated from methyl-alcoholic solution by addition of chloroform in needles, m. p. 218° (Found: N, 8·7. $C_{18}H_{20}O_4N_2$ requires N, 8·5%). Attempts to use this for the preparation of 2-nitro-4-methoxy-*m*-toluidine (compare Hadfield and Kenner, P., 1914, 253) were also unsuccessful.

2 : 4-*Dichloro*-5-*nitrotoluene*, prepared from 4-chloro-5-nitro-*o*-toluidine by the usual procedure, crystallised from alcohol in needles, m. p. 49—50° (Found: N, 6·7. $C_7H_5O_2NCl_2$ requires N, 6·8%).

5-*Nitro*-2 : 4-*dimethoxytoluene* was produced when 2 : 4-dichloro-5-nitrotoluene (4 g.) was heated for 6 hours at 115—120° with a solution of sodium (0·8 g.) in methyl alcohol (32 c.c.). It separated from light petroleum in yellow needles, m. p. 117—118° (Found: N, 7·4. $C_9H_{11}O_4N$ requires N, 7·1%).

3-*Chloro*-6-*nitro*-4-*methoxytoluene*, from 6-nitro-4-methoxy-*m*-toluidine, crystallised from alcohol in needles, m. p. 94—95° (Found: N,* 7·1. $C_8H_8O_3NCl$ requires N, 6·95%). It was converted in 6 hours by methyl-alcoholic sodium methoxide at 115—120° into 6-nitro-3 : 4-dimethoxytoluene, m. p. 119—120° (Found: N, 7·2%). De Vries (*loc. cit.*) gives 94° as the melting point.

Action of Sodium Methoxide on 2 : 5-*Dinitro*-4-*methoxytoluene*.—When the dinitro-compound (1·5 g.) was heated with a boiling solution of sodium (0·15 g.) in methyl alcohol (6 c.c.), neutrality was attained after 5 hours. The product, after four crystallisations from light petroleum (b. p. 80—110°), yielded 5-nitro-2 : 4-dimethoxytoluene (0·2 g.), m. p. 116—117°, which did not depress the melting point of an authentic specimen. In order to ascertain the actual proportion of this and its isomeride formed in the reaction, the product from another similar operation was isolated and dried in the usual manner. It solidified at 90·6°, and after the addition of 0·28 g. to 1·2 g. of the material, the solidifying point was 96°. A series of determinations of the temperatures of solidification of

mixtures of the two isomerides yielded the following results (*a* is the percentage of 6-nitro-3 - 4-dimethoxytoluene):

a.	100	91·8	83·2	76·3	66·5	60·7	55·7	54·3	51·5	51·2
s.p.....	115·5°	110·6°	105·5°	100·2°	90·7°	83·0°	78·6°	77·7°	77·6°	78·2°
a.	50·0	48·3	47·8	47·3	44·9	41·6	38·8	31·4	25·3	19·3
s.p.....	78·8°	78·0°	77·6°	77·2°	79·2°	81·7°	82·8°	87·6°	93·2°	98·6°
a.	10·2	0								
s.p.....	105·2°	113°								

From these it appears that the two isomerides combine in molecular proportion, and that the above-mentioned mixture contained 72% of 5-nitro-2 : 4-dimethoxytoluene.

3-*Nitro*-4-*methoxy*-o-*toluidine* was prepared by heating 4-chloro-3-nitro-*o*-toluidine (4·1 g.) for 6 hours at 125—130° with a solution of sodium (0·46 g.) in methyl alcohol (18·2 c.c.). The mixture was then neutral and yielded a product, which crystallised from dilute methyl alcohol in yellow needles, m. p. 61—62°. This was free from halogen and depressed the melting point of the original chloro-compound (Found: N,* 15·3. $C_8H_{10}O_3N_2$ requires N, 15·4%). Its *acetyl* derivative crystallised from benzene in needles, m. p. 176—176·5° (Found: N,* 12·6. $C_{10}H_{12}O_4N_2$ requires N, 12·5%). A solution of the base (0·5 g.) in glacial acetic acid (50 c.c.) which had been treated at 0° with a solution of sodium nitrite (2*N*; 3·4 c.c.) deposited a brownish-red precipitate after 48 hours. The product (0·44 g.), isolated by extracting the mixture with benzene, crystallised from alcohol in fine, red needles, m. p. 173—174°. Analysis showed it to be 7-*nitro*-6-*methoxyindazole* (Found: N,* 21·3. $C_8H_7O_3N_3$ requires N, 21·8%).

Action of Methyl-alcoholic Ammonia on 2 : 3-*Dinitro*-4-*methoxytoluene*.—Four separate quantities of the dinitro-compound (2·1 g.) were each treated with methyl alcohol (27 c.c.) and ammonium hydroxide (*d* 0·880; 5 c.c.) at 145—150° for 7 hours. The residue after removal of methyl alcohol by distillation was extracted with hot concentrated hydrochloric acid (400 c.c.) in order to separate unchanged material (0·5 g.) from the basic product (6·8 g.), which was recovered from the acid solution in the usual manner. When a portion of this (1·3 g.) was dissolved in glacial acetic acid (66 c.c.) and treated at 0° with sodium nitrite solution (4·5 c.c.), it yielded crude 7-nitro-6-methoxyindazole (0·35 g.), which crystallised from alcohol in red needles, m. p. 165—166°, and was identified by comparison with the authentic compound. The yield of indazole, in comparison with that attained in the preparation described above, indicated the presence of 30% of 3-nitro-4-methoxy-*o*-toluidine in the basic mixture. When a further quantity (4 g.) of this was repeatedly extracted with hot light petroleum (b. p. 40—60°), a

red solid was obtained. By crystallisation from methyl alcohol, this was obtained in orange needles (0·7 g.), m. p. 49—50° (Found : N,* 15·5. $C_8H_{10}O_3N_2$ requires N, 15·4%). Since the compound depressed the melting point of authentic 3-nitro-4-methoxy-*o*-toluidine, it was 2-*nitro*-4-*methoxy*-m-*toluidine*. Its *acetyl* derivative (Found : N,* 12·3. $C_{10}H_{12}O_4N_2$ requires N, 12·5%) crystallised from benzene in small, white needles, m. p. 170—171°, and depressed the melting point of 3-nitro-4-methoxyaceto-*o*-toluidide.

When 2 : 5-dinitrotoluene (8·4 g.) was treated in the same manner for 14 hours at 150—160°, there were obtained a black deposit (0·65 g.), unchanged material (1 g.), and red semi-solid material (2 g.), precipitated from dilute mineral acid solution, and an oily mixture of bases (2·5 g.), which furnished a semi-solid acetyl derivative.

2 : 3-*Dinitro*-4-*methoxybenzoic acid* was prepared by boiling a mixture of 2 : 3-dinitro-4-methoxytoluene (10 g.) with a solution of potassium permanganate (20 g.) and magnesium sulphate (15·6 g.) in water (900 c.c.) for 4 hours. Unchanged dinitro-compound (4 g.) was recovered, and the acid (4·9 g.) isolated in the usual manner. It crystallised from water in needles, m. p. 248—250° (decomp.) (Found : N, 11·8; equiv., 243·6. $C_8H_6O_7N_2$ requires N, 11·6%; equiv., 242). The *methyl* ester separated from methyl alcohol in needles, m. p. 156° (Found : N, 11·1. $C_9H_8O_7N_2$ requires N, 10·9%). A solution of the acid (1 g.) in methyl alcohol (15 c.c.) was heated with a solution of sodium (0·2 g.) in methyl alcohol (12 c.c.) for 14 hours at 120°; the resulting neutral solution furnished 3-*nitro*-2 : 4-*dimethoxybenzoic acid* (0·75 g.) on acidification. This crystallised from water in needles, m. p. 210—212° (Found : N,* 6·4; equiv., 225·7. $C_9H_9O_6N$ requires N, 6·1%; equiv., 227). The *methyl* ester crystallised from methyl alcohol in large prisms, m. p. 118—119° (Found : N,* 6·0. $C_{10}H_{11}O_6N$ requires N, 5·8%). The acid and its ester were shown by direct comparison to be distinct from authentic 2-nitroveratric acid, m. p. 201—202°, and its methyl ester, m. p. 127—128° (Pschorr and Sumuleanu, *loc. cit.*).

Action of Sodium Methoxide on 2 : 3-*Dinitro*-4-*methoxytoluene*.—Whether the dinitro-compound (3 g.) was heated with a solution of sodium (0·3 g.) in methyl alcohol (12 c.c.) for 8 hours at 125° or for 20 hours at 110—115°, a quantity remained unchanged and crystallised when the solution was concentrated. When the residues from a number of such experiments were fractionated, a mixture of nitrodimethoxytoluenes passed over at 132—136°/2 mm., leaving a further quantity of dinitromethoxytoluene behind. The distillate (6 g.) was completely oxidised in 4 hours by a boiling, mechanically agitated solution of potassium permanganate (16 g.) in water (800 c.c.).

The acid so obtained (4·5 g.) crystallised from water in needles, m. p. 172—177° (Found : equiv., 223·2), and on esterification furnished a mixture of methyl esters, m. p. 105—110°, from which methyl 2-nitroveratrate, m. p. 125—126°, was separated by recrystallisation from methyl alcohol. Its identity was established by direct comparison with an authentic specimen, and it was similarly shown to be distinct from methyl 3-nitro-2 : 4-dimethoxybenzoate.

THE UNIVERSITY, SYDNEY. [*Received, December 29th*, 1926.]

LXXXIX.—*Melezitose and Turanose.*

By GRACE CUMMING LEITCH.

THE discovery by Hudson and Sherwood (*J. Amer. Chem. Soc.*, 1918, **40**, 1456) that the manna found adhering to the twigs and needles of the Douglas fir consists largely of melezitose has made it possible to obtain this trisaccharide in a pure condition, and Harding (*Sugar*, 1923, 240) has shown how best to isolate the sugar from this source.

As the elucidation of the structure of this trisaccharide would solve simultaneously the problem of the structure of the reducing disaccharide turanose, an investigation was carried out by the methylation method. The conclusion was drawn that melezitose consists of two glucose residues of amylene-oxidic type united with one fructose residue of the type found in sucrose. While research on the nature of the fructose derivative was proceeding, two papers on the same topic were published by Zemplén and Braun (*Ber.*, 1926, **59**, 2230, 2539), who have arrived at a similar conclusion. Since the experimental method hereafter described differs from that of Zemplén, and since, in addition, proof is given that the fructose residue contains an oxide linking similar to that in sucrose, it was considered advisable to submit the following confirmatory evidence with regard to the nature of these two sugars.

Methylation of melezitose by the usual method with methyl sulphate and sodium hydroxide gave *hendecamethyl melezitose*, a thick syrup which could be distilled under a high vacuum. On hydrolysis with hydrochloric acid sufficiently concentrated to rupture completely the methylated trisaccharide, this syrup yielded amylene-oxidic tetramethyl glucose and trimethyl γ-fructose in the proportion 2 : 1.

Conditions of hydrolysis similar to, but slightly more drastic than, those used by Tanret (*Compt. rend.*, 1906, **142**, 1424) for the

partial hydrolysis of the unsubstituted sugar into turanose and glucose were also employed. A pure methylated turanose, however, could not be thus obtained, for scarcely any change in rotation took place as hydrolysis proceeded and therefore polarimetric observations were of little avail for detecting its completion. Tanret's method was therefore abandoned, since, during hydrolysis with hydrochloric acid, no such difficulty was encountered, and the products could be separated from each other in a pure condition by extraction of the solution with chloroform after neutralisation with barium carbonate.

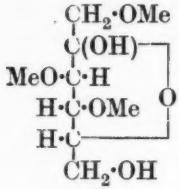
Most of the trimethyl γ-fructose remained in the aqueous solution, but some of it, together with the tetramethyl glucose, was dissolved by the chloroform. As this does not take place in the separation of tetra- and tri-methyl glucoses (Irvine and Black, J., 1926, 862; Cooper, Haworth, and Peat, *ibid.*, p. 876), the conclusion is drawn that the presence of tetramethyl glucose in an aqueous solution induces extraction of some of the trimethyl γ-fructose by chloroform, although the latter has no solvent effect on trimethyl glucose under the special conditions of the experiments. This may be due to the fact that in the one case a derivative of a γ-sugar is under investigation, whilst in the other both the tetra- and the tri-methyl glucose are of the stable or amylene-oxidic type.

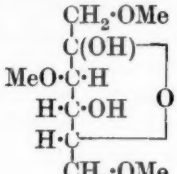
On concentration of the chloroform extract, tetramethyl glucose of the stable or amylene-oxidic type was isolated. The trimethyl fraction which remained in the aqueous solution was proved to be a ketose by the deep red coloration which it imparted to Seliwanoff's reagent (resorcinol and hydrochloric acid). It readily reduced Fehling's solution and decolorised neutral potassium permanganate in the cold. $[\alpha]_D$ in absolute ethyl alcohol, $+ 55{\cdot}5°$ (Zemplén and Braun record $[\alpha]_D + 24°$).

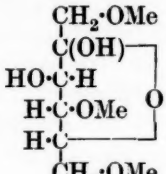
Zemplén and Braun apparently assumed that the fructose fragment of melezitose contains the same type of oxide linking as is present in the fructose of inulin and sucrose. It was obviously necessary to prove this, and the trimethyl fructose was therefore methylated with silver oxide and methyl iodide; the mobile syrup (n_D 1·4445) thus obtained gave, as the sole product of hydrolysis, a reducing sugar which agreed in physical constants with the tetramethyl γ-fructose resulting from the hydrolysis of octa- or hepta-methyl sucrose (Haworth, J., 1920, **117**, 199). This precluded the possibility of the comparatively high specific rotation of the trimethyl fructose being due to traces of tetramethyl glucose.

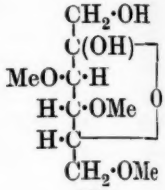
Account being taken of the recent arguments of Haworth and

Hirst (J., 1926, 1858) regarding the structure of γ-fructose derivatives, the four trimethyl γ-fructoses are :


(I.)


(II.)

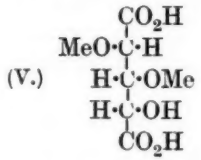

(III.)


(IV.)

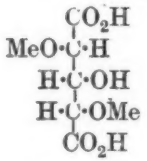
Of these, (IV) is ruled out, since turanose is capable of forming an osazone (Fischer, *Ber.*, 1894, **27**, 2486). The hydroxyl in the position next the ketose group cannot therefore be engaged in a biose linking, whence it follows that it must be methylated in the fructose fragment. In the early experiments carried out by the author, the trimethyl fructose was distilled before being analysed; the yield of trimethyl fructose which distilled was not good, and a certain proportion invariably remained as a non-volatile residue. The methoxy-content varied between 42% and 45% (Calc. for trimethyl fructose, 41·9%; for trimethoxy-anhydro-hexose, 45%). As the trimethyl fructose can be isolated in a pure condition without distillation, as seen above, this method was abandoned, but it was useful in having supplied a clue to the structure of the trimethyl fructose component. It appeared probable that distillation had resulted in the elimination of a molecule of water with consequent formation of an anhydro-fructose derivative. Anhydride formation is known to take place in 2 : 3 : 4-trimethyl glucose (Irvine and Oldham, J., 1921, **119**, 1744), which is partly converted into trimethyl glucosan on distillation. Comparison of rotation values is therefore not a trustworthy means of settling the identity of the substances under investigation, since one specimen may exist as the free sugar derivative and the other may be partly converted into an anhydro-sugar derivative.

Substances having formulæ (III) and (IV) would, on formation of anhydro-fructose derivatives, yield substances containing an ethylene-oxide linking, whilst in the product from (II) there would be present a propylene-oxide ring. No positive evidence of the existence of either of these two types of ring compounds in methylated fructose derivatives is found in the literature, whilst Haworth and Hirst (*loc. cit.*) have definitely proved that an amylene-oxide ring exists in the normal or stable type of fructose. Anhydride formation is therefore most likely where the formation of an oxide ring of this type is possible. Formula (I) admits of this, and therefore, in all probability, represents the trimethyl fructose obtained

from methylated melezitose. This deduction agrees with the experimental results of Zemplén and Braun quoted below. These authors have ruled out (III) on the ground that the reduction product of trimethyl fructose shows no alteration in rotation on addition of boric acid and therefore cannot have vicinal free hydroxy-groups. They have ascribed to trimethyl fructose formula (I), since they obtained from it by oxidation a hydroxydimethoxy-glutaric acid (V) which was not identical with authentic β-hydroxy-αα′-dimethoxyglutaric acid (VI) obtained by them by other means.

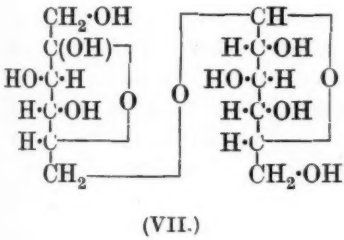


(V.)

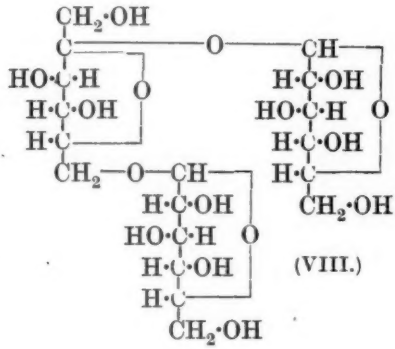


(VI.)

Turanose must therefore be represented by (VII) and melezitose by (VIII).



(VII.)



(VIII.)

Experimental.

Methylation of Melezitose. Isolation of Hendecamethyl Melezitose. —(The melezitose used in the following operations was supplied by Messrs. Baird and Tatlock, agents for The Digestive Ferments Co., Detroit, Mich., U.S.A.) Melezitose (25 g.), dissolved in the minimum volume of water, was methylated at 70° in the usual way (Haworth, J., 1915, **107**, 11) with 80 c.c. of methyl sulphate and 80 g. of 30% aqueous sodium hydroxide, care being taken to avoid acidity. The mixture was finally raised to 100° during the last half-hour of the methylation. Extraction with chloroform yielded a partly methylated syrup, which was again methylated, half-quantities of the methylating reagents being used. The chloroform extract (24 g.) was remethylated four times by Purdie's method, with excess of silver oxide and methyl iodide, 24 g. of

syrup being again obtained. This material was distilled in the vacuum of a Gaede pump; 19·5 g., b. p. 236°/0·01 mm., were then obtained [Found: OMe, 49·7; C, 52·7; H, 8·2. $C_{18}H_{21}O_5(OMe)_{11}$ requires OMe, 51·8; C, 52·9; H, 8·2%]. The distillate had n_D 1·4680, and $[\alpha]_D$ + 114° in methyl alcohol (*c*, 0·85) and + 108·6° in ethyl alcohol (*c*, 2·2). These results agree with Zemplén and Braun's $[\alpha]_D$ + 113·4° in alcohol.

Hydrolysis of Hendecamethyl Melezitose.—Method 1. This method, which was afterwards abandoned in favour of method (2) for the reason already given, consisted in applying conditions of hydrolysis similar to those employed by Tanret (*loc. cit.*) for the graded rupture of the hendecamethyl melezitose into a substituted hexose fraction and a methylated disaccharide fraction.

8 G. of an 8% solution of hendecamethyl melezitose in 20% acetic acid were hydrolysed by heating for 2 hours at 95°, the specific rotation changing from + 101·2° to + 102°. Further heating for 1 hour at 110° resulted in a further change in rotation to $[\alpha]_D$ + 103·6°. Chloroform then extracted from the mixture, neutralised by barium carbonate, 7·25 g. of a reducing syrup (n_D 1·4650). Evaporation of the aqueous solution to dryness and subsequent digestion of the barium acetate with chloroform gave no further syrup. From solubility considerations, the syrup was therefore not expected to contain any trimethyl hexose. (Tetramethyl glucose and heptamethyl turanose would both be extracted from aqueous solution by chloroform.) Distillation of the syrup remaining after removal of the chloroform gave two fractions: (1) b. p. 115°/0·3 mm. This fraction crystallised at once and was identified as tetramethyl glucose; (2) b. p. 185—190°/0·2 mm., n_D 1·4652 (Found: OMe, 46·7; C, 50·4, 50·9; H, 8·4, 8·4. Calc.: OMe, 49·3; C, 51·8; H, 8·2%).

The above figures are not in agreement with those for a heptamethyl turanose, although the two analyses agree with each other. In order to discover whether this syrup would yield tetramethyl glucose and trimethyl fructose on hydrolysis, it was heated for 1 hour at 95° with 5% hydrochloric acid. The solution had then darkened considerably and the initial rotation of + 127° had changed to + 78° and was constant. Isolation of the products followed, by the method described below, and tetramethyl glucose and a trimethyl fructose were identified.

Method 2. *Isolation of tetramethyl glucose and trimethyl γ-fructose.* Hendecamethyl melezitose (10 g.) was dissolved in 5% hydrochloric acid to give an 8% solution. After 2 hours' heating at 95°, no undue darkening of the solution had taken place and the rotation had changed from the initial value + 104° to + 70° and was constant.

The solution was diluted with water, neutralised with barium carbonate, and shaken with an excess of chloroform, whereby the syrupy product was separated into a chloroform-soluble portion (A) and a water-soluble portion (B).

Treatment of A. On removal of the solvent from solution A a syrup weighing just over 6 g. was obtained. To ensure that this was a pure tetramethyl glucose uncontaminated by trimethyl hexose, the above process was repeated, by redissolving the syrup in water and shaking the solution with small volumes of chloroform. A separation into two portions was again effected, as some of the syrup (A1) was removed from the aqueous solution under these conditions whilst the rest of the syrup (A2) was extracted only when large volumes of chloroform were used.

*The portion A*1 (trimethyl γ-fructose) weighed 1·1 g., reduced Fehling's solution, gave Seliwanoff's reaction, and had n_D 1·4670 (Found : OMe, 43·0. Calc. : 41·9%). It was therefore regarded as, in the main, trimethyl fructose.

*Treatment of A*2 (tetramethyl glucose). A2 crystallised after removal of the solvent chloroform. It was drained on porous tile, and thereafter crystallised from light petroleum in long needles, m. p. 89°; mixed m. p. with authentic tetramethyl glucose, 88° (Found : OMe, 50·7. Calc. : 52·5%). It had $[\alpha]_D$ in water (*c*, 1·7) + 91·7°, falling to + 83° (equilibrium value). The substance was therefore stable amylene-oxidic tetramethyl glucose. The yield represented approximately two-thirds of the total hydrolysed material (10 g. of hendecamethyl melezitose gave, after hydrolysis, 8·7 g. of syrup, from which 4·6 g. of tetramethyl glucose and 2·3 g. of trimethyl fructose were obtained in the pure state).

Treatment of B (trimethyl γ-fructose). The aqueous solution from the hydrolysis was carefully evaporated to dryness under diminished pressure, and the residue refluxed with chloroform. This extracted a syrup (1·2 g.) (Found : OMe, 40·0. Calc. : 41·9%), n_D 1·4660, which reduced Fehling's solution very readily and instantly decolorised neutral potassium permanganate solution. On solution in cold aqueous sodium hydroxide, it immediately developed a yellow colour; on heating, this colour deepened to dark brown. Comparative tests with fructose gave the same deepening in colour, while solutions of glucose derivatives remained pale yellow even after prolonged boiling. $[\alpha]_D$ in ethyl alcohol (*c*, 6), + 55·5°.

Methylation of Trimethyl Fructose. Isolation of Tetramethyl Methylfructoside and Tetramethyl γ-Fructose.—The trimethyl fructose was methylated with an excess of Purdie's reagents. After one methylation a non-reducing syrup (n_D 1·4445) was isolated. This was hydrolysed completely by treatment with 3% hydrochloric acid

at 95° for ½ hour. From the solution, neutralised with barium carbonate, chloroform extracted a syrup which reduced Fehling's solution strongly, had n_D 1·4540, and showed the following rotations: $[\alpha]_D$ + 24·4° in methyl alcohol (*c*, 0·9), + 29·1° in ethyl alcohol (*c*, 4·2), + 32·8° (permanent) in water (*c*, 3). These results are in agreement with the standard values for tetramethyl γ-fructose (Haworth, *loc. cit.*).

The author wishes to express her thanks to Dr. E. L. Hirst for the interest he has taken in the research.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-ON-TYNE. [*Received, February 4th*, 1927.]

XC.—*Ring-chain Tautomerism. Part XVI. The Effect of Two Adjacent* gem-*Dimethyl Groups on the Ease of Formation of the* cyclo*Pentane Ring.*

By ISRAEL VOGEL.

THE effect of the *gem*-dimethyl and other groups on the ease of formation of *cyclo*propane, *cyclo*butane, and *cyclo*pentane rings has formed the subject of numerous communications from these laboratories, but the influence of two adjacent *gem*-groups on ring formation does not appear to have been studied. The present communication deals with the effect of two adjacent *gem*-dimethyl groups on the formation of the *cyclo*pentane ring. This case is of especial interest from the point of view of the modified strain theory of Thorpe and Ingold, since the angle between the remaining two valencies of a carbon atom attached to a *gem*-dimethyl group is 109·5° (Ingold, J., 1921, **119**, 305), which differs only slightly from the angle of the normal *cyclo*pentane ring. On theoretical grounds, it would therefore be expected that in a system containing two adjacent *gem*-dimethyl groups and capable of exhibiting the phenomenon of ring-chain tautomerism, the ring isomeride would predominate; consequently the tautomerism of the substituted 1 : 6-diketone, αδ-diacetyl-ββγγ-tetramethylbutane (I), has been investigated.

(I.) $\begin{matrix}\mathrm{CMe_2\cdot CH_2\cdot COMe}\\ \mathrm{CMe_2\cdot CH_2\cdot COMe}\end{matrix}$ $\qquad$ $\begin{matrix}\mathrm{CMe_2}\text{———}\mathrm{CH_2}\\ \mathrm{CMe_2\cdot CH(COMe)}\end{matrix}\!\!>\!\mathrm{CMe\cdot OH}$ (II.)

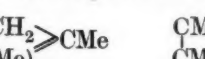
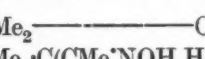
This would be expected to exist mainly in the form of the ring isomeride (II). It may be said at once that, although the mode of preparation of the compound left no doubt as to its having the open-chain formula (I) at the moment of formation, yet its properties

indicated that it reacted exclusively in the form of the ring isomeride (II). No evidence could be obtained of the existence of the open-chain compound. It is noteworthy that neither αδ-diacetylbutane, $COMe\cdot[CH_2]_4\cdot COMe$ (III) (Marshall and Perkin, J., 1890, **57**, 241) nor αδ-dibenzoylbutane, $COPh\cdot[CH_2]_4\cdot COPh$ (IV) (Wollemann, Diss., Göttingen, 1913), the simplest 1 : 6-diketones, shows any tendency to react in the ring form as would be expected from theory. Both react exclusively as diketones, although, in common with all 1 : 6-diketones, they possess a great tendency to pass into a five-membered ring by the elimination of water (compare Kipping and Perkin, J., 1889, **55**, 330; 1890, **57**, 1, 29; 1891, **59**, 214; Kipping and Mackenzie, J., 1891, **59**, 571).

The requisite 1 : 6-diketone was prepared by the reduction of mesityl oxide by moist aluminium amalgam, the reaction following the equation

$$2C_6H_{10}O + 2H = C_{12}H_{22}O_2.$$

This reduction had been previously studied by other investigators, whose results can now be readily interpreted if (II) be taken as the formula of the reduction product. Harries and Hübner (*Annalen*, 1897, **296**, 295; compare Harries and Eschenbach, *Ber.*, 1896, **29**, 380) studied the reduction of mesityl oxide by sodium and by aluminium amalgam and assigned the constitution (V) ($C_{12}H_{20}O$) to the product, although this was not in strict accordance with

(V.)   (VI.)

the analytical results, as was first pointed out by Law (J., 1912, **101**, 1016). They prepared two isomeric *mono*-oximes of the formula $C_{12}H_{20}N\cdot OH,H_2O$ to which the constitution (VI) was given. Law (*loc. cit.*) effected the reduction by an electrolytic process and obtained the same products. He was, however, able to isolate a solid which he regarded as the pure reduction product ($C_{12}H_{22}O_2$), yielding a *mono*-semicarbazone, m. p. 185—186°, and a *mono*-oxime, identical with one of the oximes prepared by Harries and Hübner. Law does not assign any definite constitution to the reduction product, but merely gives the following possible constitutional formulæ :

(*a*) $COMe\cdot CH_2\cdot CMe_2\cdot CMe_2\cdot CH_2\cdot COMe$.
(*b*) $CMe_2{:}CH\cdot CMe(OH)\cdot CMe(OH)\cdot CH{:}CMe_2$.
(*c*) $COMe\cdot CH_2\cdot CMe_2\cdot CMe(OH)\cdot CH{:}CMe_2$.

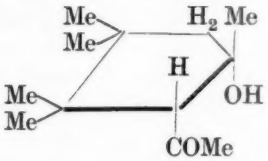
and remarks that the most probable constitution is (*c*).

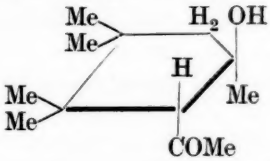
The results of the author, however, are in agreement neither with the formula of Harries and Hübner nor with those of Law,

but can be readily interpreted in terms of the constitution (II). Indeed, all the apparently divergent results of previous investigators can be simply explained by the new formula.

The reduction of mesityl oxide by moist aluminium amalgam resulted in the formation of a solid (α) and a liquid (β) form of the reduction product; the former passed into the latter on exposure to the atmosphere unless the oily liquid adhering to the solid was removed by recrystallisation. The solid form yielded a *mono*-semicarbazone, m. p. 185°, identical with that obtained by Law (*loc. cit.*), whilst the liquid also yielded a *mono*-semicarbazone, m. p. 165°. Further, the α-form yielded a *mono*-benzoyl derivative, m. p. 115°, the β-form a *mono*-benzoyl derivative, m. p. 42°, whilst tetramethylsuccinic acid resulted from both forms on oxidation with chromic acid. There appears to be little doubt that the solid and liquid forms are *cis*- and *trans*-modifications (VII) and (VIII), the α-form probably having the configuration (VII). The

(VII.)





(VIII.)

existence of two isomeric *mono*-oximes discovered by Harries and Hübner (*loc. cit.*) is in complete harmony with the above formulæ, but the constitution (VI) assigned to them by these authors must be regarded as erroneous, the correct constitutions being those represented by the oximes of the two stereoisomerides (VII) and (VIII).

The ring compound (II) is very stable towards oxidising agents. Sodium hypochlorite and potassium permanganate do not appear to have any marked effect, although with sodium hypobromite a quantitative yield of bromoform corresponding to one acetyl group was obtained, but unfortunately no other product could be isolated in sufficient quantity to admit of its complete identification. Fission of the ring took place with chromic acid and tetramethylsuccinic acid was formed.

The remarkable influence which two adjacent *gem*-dimethyl groups exert on the formation of a five-membered ring is further illustrated by the fact that all attempts to prepare the anilic acid and acid chloride of tetramethylsuccinic acid have failed, the ring anil and anhydride being invariably formed (Auwers and Gardner, *Ber.*, 1890, **23**, 3622). It is apparent that experiment fully confirms the predictions made from the modified strain theory of Thorpe and Ingold and one may assert, with some confidence, that

the production of an open-chain compound containing two adjacent *gem*-dimethyl groups will be practically if not entirely impossible should there be a possibility of the formation of a five-membered ring.

The scheme for the formation of the reduction product of mesityl oxide may be represented as follows (compare Law, J., 1912, **101**, 1016):

$$\begin{matrix} CMe_2{:}CH{\cdot}COMe \\ CMe_2{:}CH{\cdot}COMe \end{matrix} + \begin{matrix} H \\ H \end{matrix} \longrightarrow \begin{matrix} CMe_2{\cdot}CH_2{\cdot}COMe \\ CMe_2{\cdot}CH_2{\cdot}COMe \end{matrix} \longrightarrow \text{(II.)}$$

The coupling at the β-position of reduced residues has been previously observed in the reaction between moist sodium or aluminium amalgam and benzylideneacetone (Harries and Eschenbach, *Ber.*, 1896, **29**, 380), benzylideneacetophenone, phorone (Harries and Hübner, *Annalen*, 1897, **296**, 295), and other compounds (*Ber.*, 1898, **31**, 1806; *Annalen*, 1904, **330**, 235; Möller, Diss., Rostock, 1905) and more recently by Higginbotham and Lapworth (J., 1923, **123**, 1618) in the reduction of ethyl ethylidenemalonate by moist sodium amalgam. If mesityl oxide be written $Me_2\overset{+}{C}{=}\overset{-}{C}H{-}\overset{+}{C}Me{=}\overset{-}{O}$ in accordance with the theory of alternate latent polarities, it is evident that coupling takes place between carbon atoms denoted by + signs (compare Higginbotham and Lapworth, *loc. cit.*). The author is inclined to accept the mechanism (*b*) of Higginbotham and Lapworth as that which most probably represents the course of the reaction in the reduction of mesityl oxide by moist aluminium amalgam. The modified method of reduction employed results in the presentation of a very large surface to the reacting compound and one may assume that the molecules are adsorbed on the surface of the metal and actual reaction takes place in the surface, where chemical forces are known to be very powerful, according to the scheme:

$$M + \begin{matrix} CMe_2{:}CH{\cdot}COMe \\ CMe_2{:}CH{\cdot}COMe \end{matrix} \longrightarrow M\begin{matrix} CMe_2{:}CH{\cdot}COMe \\ CMe_2{:}CH{\cdot}COMe \end{matrix} \xrightarrow{2H_2O}$$

$$\overset{++}{M} + \begin{matrix} CMe_2{\cdot}CH_2{\cdot}COMe \\ CMe_2{\cdot}CH_2{\cdot}COMe \end{matrix} + 2OH^-$$

Experimental.

Preparation of Aluminium Amalgam.—200 G. of thin aluminium foil in strips about 6 inches long and 1 inch wide, loosely folded, are covered with a 10% solution of sodium hydroxide and warmed until a vigorous evolution of hydrogen has taken place for several minutes. The foil is then washed with water and with rectified

spirit, the latter operation producing an exceptionally clean surface for amalgamation. Sufficient of a 2% solution of mercuric chloride is added to cover the aluminium completely and is allowed to act for 2 minutes; it is then poured off and the amalgam is washed with water, with rectified spirit, and finally with moist ether. The amalgam is covered with about 3 litres of moist ether and is ready for immediate use. Repetition of the process is unnecessary, as it does not materially affect the yield of the reduction product.

Reduction of Mesityl Oxide. Formation of 5-Acetyl-1 : 3 : 3 : 4 : 4-pentamethylcyclopentan-1-ol (II).—Mesityl oxide (200 g.), prepared in 65% yield by the method described by Roger Adams ("Organic Syntheses," 1921, Vol. 1, p. 53), is added to the aluminium amalgam covered with moist ether in a flask fitted with two double-surface condensers. The evolution of hydrogen ceases almost immediately after the addition of the mesityl oxide and after about 20 minutes the ether boils; too vigorous ebullition must be checked by cooling the flask with running water. The reduction is usually complete after about 3 hours, and the whole is kept over-night. The ethereal solution is then filtered, and the aluminium hydroxide sludge washed with ether. The ethereal solution is dried with calcium chloride, and the ether evaporated. The crude reduction product (about 200 g.), which has an odour which can best be described as that of a mixture of camphor and peppermint, is fractionated as rapidly as possible, since prolonged heating tends to cause the partial elimination of water from the primary reduction product. Further, it is advisable to carry out the fractionation as soon as possible after the completion of the reduction, as standing in contact with even a small quantity of dry ether produces a considerable quantity of high-boiling material, which was not investigated. The bulk of the liquid distils at 119—126°/20 mm., and a small quantity at 138—140°/20 mm. The main fraction, on long standing and strong cooling, deposits a crystalline solid soluble in most organic solvents. Law (J., 1912, **101**, 1016) was unable to find a medium for recrystallisation and records the m. p. of the crude solid as 53—55°. It can, however, be readily crystallised from a mixture of light petroleum (b. p. 40—60°) and ether and has, after one recrystallisation, m. p. 45°, which remains constant even after five recrystallisations. The solid, if not quickly recrystallised, passes into the liquid form on exposure to the atmosphere for several days (Found for solid, m. p. 45°: C, 72·7; H, 11·0. Found for the liquid, b. p. 122—124°/20 mm.: C, 72·6; H, 11·2. $C_{12}H_{22}O_2$ requires C, 72·7; H, 11·0%).

The *semicarbazone* of the solid form is formed after some standing and crystallises from alcohol in hard prisms, m. p. 185° (Found:

C, 60·0; H, 9·3; N, 18·7. $C_{13}H_{25}O_2N_3$ requires C, 59·8; H, 9·6; N, 18·4%). No disemicarbazone could be detected.

The *semicarbazone* of the liquid form, prepared in the usual manner, after several recrystallisations from methyl alcohol, melts constantly at 165° (Found : N, 18·6%). No trace of a disemicarbazone could be detected.

The *benzoyl* derivative of the solid form is prepared by dissolving 1 g. of the solid in 4 g. of pure pyridine and slowly adding 1·5 g. of freshly-distilled benzoyl chloride. The colour of the solution gradually darkens and after ½ hour the whole is poured into excess of dilute hydrochloric acid (1 : 1). The yellowish-brown oil produced is isolated by means of ether (the ethereal solution being washed with dilute sodium bicarbonate solution and with water and dried with sodium sulphate) and solidifies after being kept in a vacuum desiccator for 2 months. It crystallises from methyl alcohol in lustrous plates, m. p. 115° (Found : C, 75·3; H, 8·5. $C_{19}H_{26}O_3$ requires C, 75·5; H, 8·6%).

The *benzoyl* derivative of the liquid form is prepared in a similar manner, except that the benzoyl chloride is added to the pyridine solution cooled to − 5° and the whole is kept for 2 days. The yellowish-brown oil thus obtained solidifies when a small quantity of the oil is removed by distillation in a vacuum. The monobenzoyl derivative separates from a mixture of light petroleum (b. p. 40—60°) and sodium-dried ether in thick needles, m. p. 42° (Found : C, 75·4; H, 8·4. $C_{19}H_{26}O_3$ requires C, 75·5; H, 8·6%).

Oxidation with Sodium Hypobromite.—The procedure of Baeyer (*Ber.*, 1896, **29**, 25) is followed for the oxidation of the liquid fraction, b. p. 120—125°/20 mm. A quantitative yield of bromoform corresponding to one acetyl group is obtained, but the only oxidation product which can be isolated consists of a small quantity of viscid gum. A portion crystallises after several months and melts at 122—123°. The acid yields sparingly soluble silver and barium salts, but sufficient could not be isolated to admit of its full characterisation.

Oxidation with Nitric Acid.—The only product which can be isolated by the oxidation of the liquid, b. p. 120—125°/20 mm., by concentrated nitric acid is oxalic acid.

Oxidation with Potassium Permanganate.—The substance is scarcely affected by permanganate.

Oxidation with Chromic Acid.—10 G. of the liquid, b. p. 120—126°/20 mm., are dissolved in 160 c.c. of glacial acetic acid, and a solution of 100 g. of chromic acid in 160 c.c. of 50% acetic acid is added. After the initial vigorous reaction has subsided, the mixture is refluxed for 1 hour. The product is distilled in steam until the

distillate is no longer acid; the distillate is extracted six times with ether, and the ethereal extract dried with anhydrous sodium sulphate. The residue, after removal of the ether, consists of a solution of the oxidation product in acetic acid. The latter is almost completely removed by distillation in a vacuum; a crystalline acid, m. p. 198° (rapid heating), is then obtained. Its identity with tetramethylsuccinic acid was established by analysis (Found: C, 55·1; H, 8·0. Calc.: C, 55·2; H, 8·0%) and by conversion into the anil.

The anil of tetramethylsuccinic acid is obtained by heating 0·4 g. of the acid (m. p. 198°) with 0·4 g. (2 mols.) of freshly distilled aniline to the boiling point for a few moments; the whole solidifies on cooling in ice. The excess of aniline is removed by washing with dilute hydrochloric acid. The anil (0·5 g.) separates from dilute alcohol in colourless needles, m. p. 87—88° (compare Auwers and Gardner, *Ber.*, 1890, **23**, 3622; Auwers, *Annalen*, 1896, **292**, 176, who give m. p. 88°) (Found: N, 6·2. Calc.: N, 6·1%).

Identical results are obtained on oxidation of the solid form of the reduction product with chromic acid under similar conditions.

In conclusion, I wish to express my indebtedness to the Chemical Society for a grant which has partly defrayed the expenses incurred in the research, and to Prof. J. F. Thorpe, F.R.S., and Dr. E. H. Farmer for their kind interest in this investigation.

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XCI.—*The Influence of Groups and Associated Rings on the Stability of Certain Heterocyclic Ring Systems. Part I. The Substituted Glutarimides.*

By SARBBANI SAHAY GUHA SIRCAR.

THE modified strain theory developed by Thorpe and Ingold to explain the relative stabilities of various ring systems has on the whole received ample general experimental confirmation by the work of these and other workers. Their investigations, however, with few exceptions, involved experimental conditions of such a drastic nature that the quantitative comparison of the stabilities of the various systems was a matter of considerable difficulty, and frequently corrections had to be applied for one or more side-reactions which were difficult to control. Though these phenomena were successfully unravelled by these chemists, the difficulty in the

way of the ideal solution of the problem could not fail to be noticed. This difficulty was partly solved by Ingold, Sako, and Thorpe (J., 1922, **121**, 1177) by studying the hydrolysis under mild conditions of a number of substituted hydantoins; but the necessary variety of substituted hydantoins is not easy to obtain. Moreover, although the work on hydantoins brought forward strong evidence in support of the modified strain theory, it seemed remarkable that the influence of the substituents was completely unaffected by the presence of two nitrogen atoms in the ring, the valency direction of each of which could not fail to be affected in the same way by the substituents. In other words, the disturbing factors introduced by the nitrogen atoms and the carbonyl groups made the problem more complicated than was desirable.

It was considered that heterocyclic rings, such as imides, anhydrides, and lactones, which are opened under mild conditions without complicated side-reactions, would be more suitable for a quantitative study of ring stability. Although a considerable amount of work has been done on the stability of anhydrides by Voermann, Rivett and Sidgwick, Böeseken and his collaborators, and by Verkade and Hjelt, it affords no substantial contribution towards a solution of the present problem.

Sporadic studies of the hydrolysis of a few imides by Miolati (*Atti R. Accad. Lincei*, 1894, **3**, i, 515; 1896, **5**, ii, 375) and of a few lactones by Hjelt (*Ber.*, 1891, **24**, 1236) and by Henry (*Z. physikal. Chem.*, 1892, **10**, 96) throw but little light on the subject under discussion.

The method employed by Miolati and by Henry has now been utilised to work out the comparative rates of hydrolysis of the ring systems mentioned above. It is hoped that by studying the various combinations of the carbon atoms, the carbonyl group, and the hetero-atom, some information may be obtained on the actual effect of the substituting hydrocarbon radicals unaffected by other factors.

The evidence thus obtained from the hydrolysis experiments points unmistakably to the well-marked influence of the substituents in modifying the stability of the various systems in the direction indicated by the modified strain theory. The fact that the ring opens at the hetero-atom, and not at any of the carbon atoms of the ring, probably diminishes the effective manifestation of the molecular strain contributed, if at all, by the distortion of the bonds of the nitrogen or the oxygen atom, unless we assume that the bonds of atoms with "residual valency" may be of a more pliant and accommodating nature than carbon bonds are known to be. This discussion will be amplified, however, in a future communication.

The present paper is concerned with a study of the velocity of hydrolysis of a number of substituted glutarimides, the various substituents being H,H; Me,H; Et,H; Me,Me; Me,Et; Et,Et; *cyclo*pentane, and *cyclo*hexane. In the presence of dilute caustic soda, the reaction

$$\begin{matrix} R \\ R_1 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CH_2\cdot CO \\ CH_2\cdot CO \end{matrix}\!\!>\!NH + NaOH = \begin{matrix} R \\ R_1 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CH_2\cdot CO_2Na \\ CH_2\cdot CO\cdot NH_2 \end{matrix}$$

was found to be bimolecular, having a suitable velocity at 25°. Complications due to side reactions took place if the reaction was prolonged beyond the early stages. Another disturbing factor is the presence in the imide of traces of the free acid, which in the form of its salt has a great catalytic influence on the hydrolysis, the velocity being increased at a rate out of all proportion to the amount of the impurity. This factor was responsible for a number of anomalous results in the preliminary experiments, but was eliminated by more thorough purification of the imides.

The following table shows how closely the experimental data agree with the expectations of the modified strain theory, and also indirectly justifies the method here adopted. The full significance of the actual coefficients is not easy to explain. In the table, 2θ represents the calculated angle between two of the carbon bonds and k represents the velocity coefficients of the reactions.

Substituents.	2θ.	$10k$.	Substituents.	2θ.	$10k$.
H,H	115·3°	0·247	Me,Et	?	0·0124
Me,H	112·5	0·0725	Et,Et	?	0·00435
Et,H	?	0·158	*cyclo*Pentane	107·2°	0·00275
Me,Me	109·5	0·0127	*cyclo*Hexane	105·2	0·00215

Experimental.

Preparation of the Imides.—All the imides were prepared by distilling the dry ammonium salt of the appropriate acid from a small retort under ordinary pressure. A large, smoky flame was used and superheating was avoided, the imides being thus obtained in good yield. They were purified by crystallisation from acetone–ether, and then from hot water, being undecomposed by such treatment. Most of the imides are known, but the di-substituted ones had not previously been prepared by the above method. The m. p.'s of the already-known imides agreed completely with those recorded in the literature. As all the glutaric acids are known, details of their preparation are omitted.

Hydrolysis.—95 C.c. of a $N/190$-solution of the imide (actual weights shown at the head of each table) were placed in a 300 c.c. flask and kept in a thermostat at 25° (± 0·2°). When the solution had attained the temperature of the thermostat, 5 c.c. of $N/10$-sodium hydroxide solution were introduced by means of a pipette

and the mixture was well stirred. After 1 minute, portions of 10 c.c. were removed at intervals of 5—10 minutes (depending on the velocity of the reaction), run into about 15 c.c. of ice-cold distilled water, and the unused alkali was titrated with $N/100$- or $N/200$-sulphuric acid. The velocity coefficient was calculated from the formula for a bimolecular reaction $k = x/ta(a - x)$, where t is the time (in minutes), a the initial concentration of imide (corresponding to 10 c.c. of $N/200$-, or 5 c.c. of $N/100$-acid), and x the alkali utilised. No great accuracy is claimed where the velocity is high, but the number of such cases is small. The results of the experiments are given in the Tables I—VIII, the figures in the second column representing c.c. of $N/100$-(or $N/200$-)acid used in the titration.

Glutarimide (see Table I).—Yield, 65·4%. It was crystallised first from acetone and then from water; glistening scales, m. p. 152° (Found: N, 12·1. Calc.: N, 12·4%).

TABLE I.

0·1486 g. dissolved in 250 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	4·2	—
5	2·2	0·0254
10	1·5	0·0233
15	1·05	0·0256
20	0·95	0·0244
27	0·65	0·0248
33	0·55	0·0243
	Mean	0·0247

(Miolati obtained 0·0251.)

TABLE II.

0·1672 g. dissolved in 250 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	4·6	—
5	3·5	(0·0086)
10	2·95	0·0070
15	2·4	0·0072
20	2·05	0·0072
25	1·75	0·0074
30	1·5	0·0074
	Mean	0·00725

β-*Methylglutarimide* (see Table II).—Yield, 68%; crystallised from ether–acetone in scales, m. p. 142—143° (Found: N, 11·3. Calc.: N, 11·0%).

β-*Ethylglutarimide* (see Table III).—Yield, 57%; crystallised from acetone–ether and then from water; scales, m. p. 87° (Found: N, 10·3. Calc.: N, 9·9%).

TABLE III.

0·0742 g. dissolved in 100 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	3·2	—
5	2·4	(0·0216)
10	1·8	0·0177
15	1·425	0·0167
20	1·25	0·0166
25	1·05	0·0150
30	0·90	0·0133
35	0·825	0·0192
	Mean	0·0158

TABLE IV.

0·1854 g. dissolved in 250 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	4·85	—
5	4·05	—
10	4·40	0·00136
15	4·15	0·00136
20	3·95	0·00133
25	3·75	0·00133
30	3·7	0·00117
43	3·45	0·00104
	Mean	0·00127

ββ-*Dimethylglutarimide* (see Table IV).—Yield, 75%; crystallised from water in long needles, m. p. 147° (Found: N, 10·3. $C_7H_{11}O_2N$ requires N, 9·9%).

ββ-*Methylethylglutarimide* (see Table V).—Yield, 70%; crystallised from water in leafy plates, m. p. 127° (Found: N, 9·3. $C_8H_{13}O_2N$ requires N, 9·0%).

TABLE V.

0·0816 g. dissolved in 100 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	4·8	—
5	4·7	0·00127
10	4·4	0·00136
15	4·2	0·00127
20	3·95	0·00132
25	3·8	0·00126
30	3·7	0·00117
35	3·65	0·00105
	Mean	0·00124

TABLE VI.

0·0846 g. dissolved in 95 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	4·95	—
5	4·85	(0·000618)
10	4·8	0·000416
20	4·6	0·000434
30	4·45	0·000412
40	4·2	0·000476
50	4·1	0·000439
	Mean	0·000435

ββ-*Diethylglutarimide* (see Table VI).—Yield, 48%; crystallised in glistening plates from water; m. p. 146—147° (Found: N, 8·0. $C_9H_{15}O_2N$ requires N, 8·2%). Owing to its sparing solubility, 0·0846 g. (corresponding to 95 c.c. of N/190-solution) of the finely powdered imide was suspended in 95 c.c. of distilled water and kept at 25°; 5 c.c. of N/10-sodium hydroxide solution were added, and the imide then dissolved in 5 minutes.

cyclo*Pentanediacetimide* (see Table VII).—Yield, 68%; crystallised in plates from acetone or water, m. p. 153—154° (Found: N, 8·2. $C_9H_{13}O_2N$ requires N, 8·4%).

TABLE VII.

0·2198 g. dissolved in 250 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	5·1	—
5	4·90	—
10	4·85	0·000309
20	4·75	0·000263
30	4·65	0·000252
40	4·55	0·000297
50	4·425	0·000261
60	4·3	0·000271
	Mean	0·000275

TABLE VIII.

0·1814 g. dissolved in 95 c.c.; $a = 5·0$.

t.	$a - x$.	k.
0	5·0	—
5	4·85	—
10	4·85	0·000309
20	4·8	0·000209
30	4·7	0·000212
40	4·6	0·000217
50	4·5	0·000220
60	4·425	0·000216
	Mean	0·000215

cyclo*Hexanediacetimide* (see Table VIII).—Yield, 70%; crystallised from water in glistening scales, m. p. 169° (Found: N, 7·5. $C_{10}H_{15}O_2N$ requires N, 7·7%).

Summary.

The velocity coefficients for the hydrolysis of a number of substituted glutarimides have been studied with the view of finding how far the order of stability in this series of compounds agreed with the expectations of Thorpe and Ingold's modified strain theory. The agreement is quite satisfactory. The unusual instability of glutarimide itself is very marked, and the effect of the methyl group in increasing the stability is also remarkable. After that, however, there is a steady increase of stability as the series is ascended (H,H; Me,H; Et,H; Me,Me; Me,Et; Et,Et; *cyclo*pentane; *cyclo*hexane).

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XCII.—*The Platini-Platino-chloride Electrode. A New Type of Chlorine Electrode.*

By VIRGINIA F. MILLER and HENRY TERREY.

AN inert electrode in a solution of sodium chloroplatinate and sodium chloroplatinite acquires a definite potential. The mechanism of the electrode differs from that of the usual oxidation–reduction type in that there is no change in valency. Measured against a calomel electrode, the platinum of the platini-platino electrode is positive to the mercury. The cell reaction is expressed by

$$2Hg + Na_2PtCl_6 \longrightarrow 2HgCl + Na_2PtCl_4 \quad . \quad . \quad (1)$$

the current passing from left to right inside the cell:

$$\bar{Hg} \mid Hg_2Cl_2,NaCl \mid NaCl + Na_2PtCl_6 + Na_2PtCl_4 \mid \dot{Pt}.$$

The electrode reaction is

$$\bar{\bar{P}}t\bar{\bar{C}}l_6 + 2e \longrightarrow \bar{\bar{P}}t\bar{\bar{C}}l_4 + 2\bar{C}l$$

and the *E.M.F.* is given by

$$E = E_0 + RT/2F \,.\, \log [\bar{\bar{P}}t\bar{\bar{C}}l_6]/[\bar{\bar{P}}t\bar{\bar{C}}l_4][\bar{C}l]^2,$$

or, more exactly, by

$$E = E_0 + RT/2F \,.\, \log a_i/a_o a^2_{Cl} \quad . \quad . \quad . \quad . \quad (2)$$

where a_i, a_o, and a_{Cl} are the activities of the chloroplatinate, the chloroplatinite, and the sodium chloride, respectively.

To test the above relationship, two series of measurements were carried out. In the first, the chloride concentration was kept constant and the $i : o$ ratio varied. In the second, this ratio was constant and the chloride concentration varied. (Here, i and o represent the total concentrations of chloroplatinate and chloroplatinite, respectively.)

The values of E_0 calculated according to the above expression for the two series of measurements are given in Table I (full data in Tables II and III). Since the concentration of sodium chloride is much higher than those of the platinum salts, the ratio of the activities of the latter was assumed to be equal to the ratio of their concentrations, *i.e.*, $a_i/a_o = i/o$. The activity of the chlorine ion was taken to be the same as in the corresponding sodium chloride solution.

TABLE I.

Series I.			Series II.		
$i : o$ ratio.	NaCl (mols./litre).	E_0 (volts).	$i : o$ ratio.	NaCl (mols./litre).	E_0 (volts).
0·5804	1	0·7191	1·4642	1·0000	0·7202
0·9199	,,	0·7217	,,	0·7000	0·7184
1·4642	,,	0·7202	,,	0·5000	0·7176
2·0441	,,	0·7211	,,	0·2000	0·7173
2·9282	,,	0·7206	,,	0·1000	0·7165
5·3773	,,	0·7210	,,	0·0500	0·7143
11·8033	,,	0·7213	,,	0·0100	0·7060
29·5633	,,	0·7211	,,	0·0048	0·6985

It will be seen that with constant sodium chloride concentration a satisfactorily constant value for E_0 is obtained. The value, however, changes slightly with change in the sodium chloride environment. This suggests that the ratio of the activities of the chloro-platinate and -platinite ions is not independent of the surroundings and that this ratio should be expressed as a function of the sodium chloride concentration, *i.e.*, $a_i/a_o = K \,.\, i/o$, where K is a function of the ionic strength of the sodium chloride * solution. When K is constant, this leads to the expression

$$E = (E_0 + RT/2F \,.\, \log K) + RT/2F \,.\, \log (i/o) - RT/F \,.\, \log a_{Cl} \quad . \quad . \quad . \quad (3)$$

the given values of E_0 in Series I being really values of

$$(E_0 + RT/2F \,.\, \log K),$$

where K corresponds to M-sodium chloride solution.

* At low concentrations of sodium chloride it would possibly be preferable to use the total ionic strength of the solution instead of that of the sodium chloride alone.

If the values of E in Series II are plotted against a_{Cl}, a straight line is obtained for the first six values. A straight line would result if $\log K$ were itself a linear function of $\log a_{Cl}$, *i.e.*, if $\log K = \alpha + \beta \log a_{Cl}$, where α and β are constants.

Making this assumption, we have

$$E = E_0 + RT/2F \,.\, (\beta - 2) \log a_{Cl} + RT/2F \,.\, \log i/o + RT/2F \,.\, \log \alpha$$

$$\text{or } E = (E_0 + C) + RT/2F \,.\, (\beta - 2) \log a_{Cl} + RT/2F \,.\, \log i/o \quad (4)$$

where C is an undetermined constant which cannot be evaluated until the nature of K is known. As will be seen later, this expression gives a satisfactorily constant value for $(E_0 + C)$.

Experimental.

The sodium chloroplatinate was obtained by dissolving platinic chloride in sodium chloride and crystallising the hexahydrate. The chloroplatinite was made by converting platinum tetrachloride into dichloride by heating at 350° and dissolving the residue in hydrochloric acid. This solution was neutralised with barium carbonate, and on evaporation gave dark red crystals of $BaPtCl_4,3H_2O$, contaminated with a little barium chloride. Treatment of this salt with sodium sulphate gave the corresponding sodium salt; owing to its high solubility it was impossible to purify it by crystallisation (Found: H_2O, 12·11; NaCl, 8·01; Na_2PtCl_4, 79·88%). Since, however, sodium chloride was used as the electrolyte, the removal of the small amount present as impurity was unnecessary. In making up the solutions the sodium chloroplatinite was weighed anhydrous. Except for solutions 6, 7, and 8 of the first series and for the more concentrated platinum solutions, the electrode mixtures were made by adding 3—10 c.c. of a stock solution to the required amount of sodium chloride and then diluting to 25 c.c. Solutions 6, 7, and 8 were made by taking weighed amounts of the two salts.

The Cell.—The electrode vessels were of the type commonly used for single electrodes, with a tap sealed in the connecting tube to prevent diffusion. The electrode was measured against a normal calomel electrode containing sodium chloride instead of potassium chloride. Platinised glass was found to be the most suitable form of electrode, equilibrium being established after about 24 hours. The cells were measured at 25°, an air thermostat being used to control the temperature. The measuring apparatus consisted of a Pye potentiometer, a Cambridge Instrument Company moving-coil galvanometer, and a Cambridge standard cadmium cell.

Results.

After attainment of equilibrium, readings varied by less than 0·1 millivolt over a period of several hours, except in the case of the 0·2*N*-sodium chloride solution, where the variation from the mean over 6 hours was 0·6 millivolt. The values were tested for reproducibility. For solution 8 of the first series, the first sample gave a mean value of 0·5057, with no variation in the readings in 8 hours after attainment of equilibrium; the second sample gave a mean value of 0·5057, the readings varying from 0·5056 to 0·5058.

The effect of change in the values of i and o with a constant ratio between them was as follows, the sodium chloride concentration being N.

i (mol./litre).	o (mol./litre).	$i : o$.	*E.M.F.* of cell.
(*a*) 0·005548	0·009559	0·580	0·4549
(*b*) 0·0005548	0·0009559	0·580	0·4532

A solution with concentrations one-tenth of those in (*b*) did not give constant readings.

Table II gives the results of the first series of readings in N-sodium chloride solution. The value used for the calomel electrode potential was 0·2731 volt. Table III gives the results of the second series of measurements, in which a liquid potential was introduced between the connecting liquid and the electrode solution, diminishing the *E.M.F.* measured. This potential was calculated from the relationship

$$E_L F = (n_k - n_a) RT \log C_1\alpha_1/C_2\alpha_2$$

where E_L is the liquid potential, n_k and n_a are the transport numbers of the kation and anion, respectively, and α_1 and α_2 are the activity coefficients of the sodium chloride solutions.

The calculation of β in equation (4) was carried out by taking the values of E found in experiments 2 and 6 (Table III), whence, by subtraction,

$$(E_2 - E_6) = RT/2F \,.\, (\beta - 2)[\log (a_{Cl})_6 - \log (a_{Cl})_2]$$

and hence $\beta = 0{\cdot}1317$.

The Effect of Temperature on the E.M.F. *of the Electrode.*

The potentials of solutions 6 and 7 of the first series were measured at 21°, 25°, and 30°, with the following results :

$i : o$.	*E.M.F.* (volt) of electrode.		
	21°	25°	30°
(6) 5·3773	0·7532	0·7537	0·7537
(7) 11·8033	0·7627	0·7641	0·7642

Table II.

Cell $\overline{Hg}\,|\,Hg_2Cl_2$, N-NaCl $|$ N-NaCl + Na_2PtCl_6 + $Na_2PtCl_4\,|\,\overset{+}{Pt}$. Temperature 25°.
($a_{Cl} = 0{\cdot}650$.)

No.	$i \times 10^3$ (mols./litre).	$o \times 10^3$ (mols./litre).	$\frac{i}{o}$.	*E.M.F.* cell.	*E.M.F.* electrode, E.	$\frac{RT}{2F}(\beta-2)\log a_{Cl}$.	$\frac{RT}{2F}\log\frac{i}{o}$.	$E_0 + C$.
1	0·5548	0·9559	0·5804	0·4532	0·7232	0·01035	−0·0070	0·7199
2	0·9187	0·9987	0·9199	0·4617	0·7317	0·01035	−0·0011	0·7225
3	1·4623	0·9987	1·4642	0·4662	0·7362	0·01035	0·0049	0·7209
4	2·041	0·9987	2·0441	0·4714	0·7414	0·01035	0·0092	0·7218
5	2·9243	0·9986	2·9282	0·4751	0·7455	0·01035	0·0138	0·7213
6	5·3703	0·9987	5·3773	0·4837	0·7537	0·01035	0·02163	0·7218
7	11·789	0·9987	11·8033	0·4941	0·7641	0·01035	0·0317	0·7220
8	29·524	0·9987	29·5633	0·5057	0·7757	0·01035	0·0436	0·7218
							Mean	0·7215

Table III.

$i : o$ = constant = 1·4642. Temperature 25°.

Cell $\overline{Hg}\,|\,Hg_2Cl_2$, N-NaCl $|$ xNaCl + 0·001462 Na_2PtCl_6 + 0·0009987 $Na_2PtCl_4\,|\,\overset{+}{Pt}$.

NaCl (mols./litre).	a_{NaCl}.	a_{NaCl}.	*E.M.F.* cell.	*E.M.F.* electrode, E_1.	Liquid potential, E_2.	$E_1 + E_2$. (E).	$\frac{RT}{2F}(\beta-2)\log a_{Cl}$.	$\frac{RT}{2F}\log\frac{i}{o}$.	$E_0 + C$.
1·0000	0·650	0·650	0·46615	0·7362	0·0000	0·7362	0·01035	0·0049	0·7209
0·7000	0·673	0·471	0·47099	0·7410	0·0016	0·7426	0·0181	0·0049	0·7196
0·5000	0·689	0·344	0·47665	0·7467	0·0032	0·7499	0·0256	0·0049	0·7194
0·2000	0·752	0·150	0·49353	0·7635	0·0073	0·7707	0·0455	0·0049	0·7203
0·1000	0·798	0·0798	0·50580	0·7758	0·0105	0·7863	0·0602	0·0049	0·7213
0·0500	0·842	0·0421	0·51694	0·7869	0·0137	0·8006	0·0761	0·0049	0·7196
0·0100	0·922	0·00922	0·5400	0·8100	0·0213	0·8313	0·1126	0·0049	[0·7138]
0·00479	0·940	0·00450	0·5473	0·8173	0·0250	0·8423	0·1298	0·0049	[0·7076]
								Mean	0·7202

* In the first series $dE/dT = 0{\cdot}000033$; in the second $dE/dT = 0{\cdot}000084$. At 25° the *E.M.F.* of the cell is 0·4837 and 0·4941 in the two series. Applying the Gibbs–Helmholtz equation, $nFE - Q = nFTdE/dT$ (where Q is the heat evolved in the cell-reaction at constant temperature and pressure), to these data we obtain

$$Q = 21{,}830 \text{ cals. from 1st series}$$
$$21{,}610 \text{ ,, ,, 2nd ,,}$$

The heat of formation of 2HgCl = 62,600 cals. and thus the heat of formation of Na_2PtCl_6 from Na_2PtCl_4 and Cl_2 is seen from the equation (1) for the cell-reaction to be 40,770 cals. (1st series), 40,990 cals. (2nd series). We may compare this value with that of Thomsen from direct heat measurement, *viz.*, 42,000 cals.

Summary.

The potential of the platini-platino-chloride electrode has been measured. The *E.M.F.* varies according to the equation

$$E = (E_0 + C) + RT/2F \,.\, (\beta - 2) \log a_{Cl} + RT/2F \,.\, \log i/o$$

where β and C are constants.

The temperature coefficient of the cell was determined. From the Gibbs–Helmholtz equation the heat of formation of sodium chloroplatinate from the chloroplatinite and chlorine was calculated as 40,880 cals.

Our best thanks are due to Professor Donnan for his advice and help.

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XCIII.—*The Viscosity of Ether at Low Temperatures.*

By EBEN HENRY ARCHIBALD and WILLIAM URE.

As explained in a former paper (J., 1924, **125**, 726), we wished to know the rate of change of viscosity with temperature of certain organic liquids at low temperatures. The viscosity of acetone has been investigated (*loc. cit.*). The present experiments deal with the viscosity of ethyl ether over a temperature range of 0° to — 110°, the measurements being made at 10° intervals.

* These are the values of dE/dT at 25° determined graphically from the *E.M.F.*–temperature curve.

Materials and Apparatus.—"Anhydrous ether distilled over sodium" was treated with three successive portions of water to remove alcohol, dried over calcium chloride, then over sodium and distilled.

The Ostwald type of viscometer was used and the apparatus was set up as shown in Fig. 1. To prevent atmospheric moisture from condensing in the viscometer both ends were connected to calcium chloride drying tubes. Careful observation convinced us that no difference in the time of flow was caused by inserting these tubes. The required volume of ether was transferred from a supply flask by means of a syphon, one end of which passed into

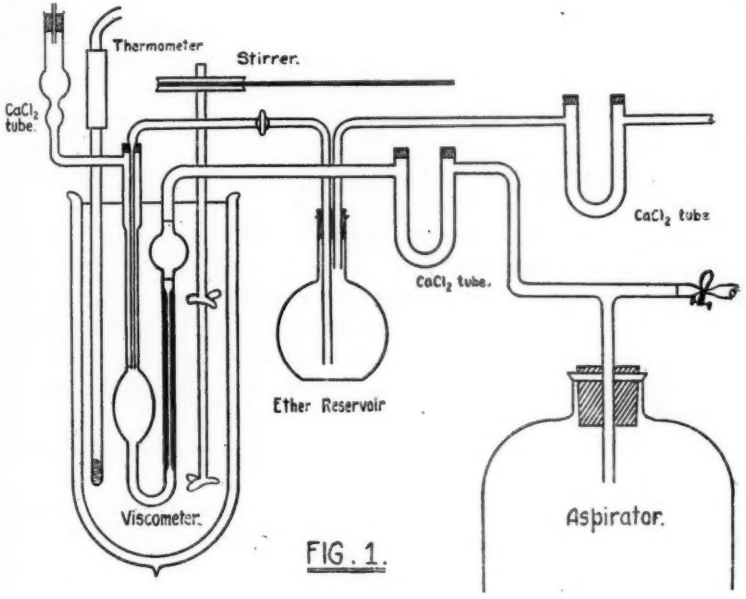


FIG. 1.

the larger end of the viscometer. The liquid was drawn up to the graduation above the bulb by means of an aspirator.

The cryostat consisted of a large unsilvered Dewar tube of about 10 cm. internal diameter which was almost filled with dry ether. For measurements from 0° to — 75° carbon dioxide snow was used to regulate the temperature, small amounts being added at intervals. Below — 75°, liquid air was used, and was handled after the manner devised by Henning (*Z. Instrument.*, 1913, **33**, 33).

The temperatures were indicated by a platinum resistance thermometer of the bridge type, Leeds and Northrop Meter Bridge, No. 4201, being used, reading to 0·0001 ohm, corresponding to about 0·01°. The resistance element was contained in a quartz

tube which also contained gold compensating leads. The galvanometer was observed with lamp and scale. The resistance of the leads was eliminated by taking the mean of two readings at opposite positions of the commutator switch.

The thermometer was standardised by the Bureau of Standards in September 1923, and δ in the Callendar equation was found to be 1·50. On installation in this laboratory, the thermometer was checked at 0°, and observations were made at the temperatures of the ether and solid carbon dioxide mixture (— 78·34° at atmospheric pressure) and of boiling oxygen (— 182·95°) to determine the deviation from the parabolic formula. At — 78·34°, the thermometer read 0·04° low and at — 182·95°, 1·77° low. These values correspond to Henning's corrections to the parabolic formula (*Ann. Physik*, 1913, **40**, 735), and these corrections were accordingly used. A resistance-temperature chart was plotted and used to obtain the temperatures at which the viscosity measurements were made.

At the higher temperatures, the cryostat could be controlled within 0·1°, and below — 30° within 0·2°.

For measurements between 0° and — 30°, a viscometer having a very fine capillary was used. The water rate at + 20° was 385·2 sec., and the maximum time of flow of ether was 211·2 sec. at — 32·1°. At the lower temperatures, a tube of somewhat larger bore was employed. The water rate in this case was 207·6 sec. at 0° and the maximum time of flow for the ether 341·2 sec. at — 109·8°.

By means of a stop watch, the time of flow could be measured to within 0·2 sec.

Results.—The viscosities were calculated from the observed times of flow in the same manner as in the previous paper (*loc. cit.*) using the equation

$$\eta = \frac{dt}{d_w t_w}\left(\eta_w + \frac{m d_w V}{8\pi l t_w}\right)\{1 - 0{\cdot}000008(0 - t)\} - \frac{m d V}{8\pi l t},$$

where η is the coefficient of viscosity of the liquid, V the volume of liquid which flows through the capillary in the time t, d the density of the liquid, l the length of capillary, and m a constant = 1·12 (Boussinesq, *Compt. rend.*, 1891, **112**, 1099); those symbols with subscript w relate to water.

This expression includes corrections for kinetic energy and for the change in the dimensions of the instrument with temperature. The density values were taken from the work of Taylor and Smith (*J. Amer. Chem. Soc.*, 1922, **44**, 2456).

The results are given in Table I, in which the viscosities are

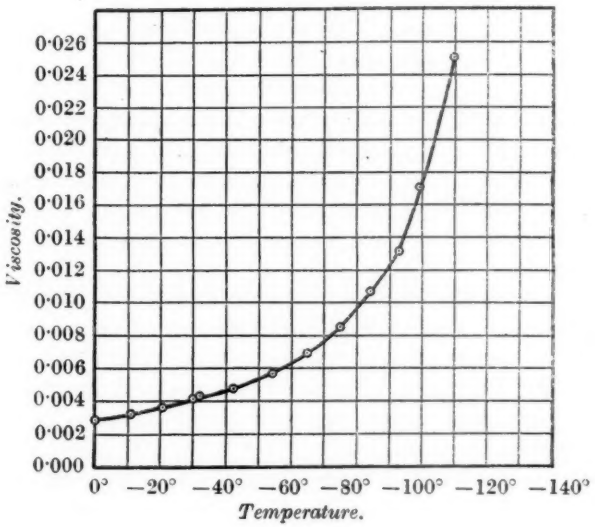
expressed in absolute units, that of water at 0° being taken as 0·01792. In most cases, they are given to four significant figures, which is the accuracy warranted by the time measurement and temperature control. Where the time of flow was relatively short or the agreement in a series of measurements not close, the results are given to only three significant figures. For completeness, the densities at the various temperatures are included in the table.

TABLE I.

Temp.	d.	η.	Temp.	d.	η.
0·0°	0·73629	0·002903	— 64·5°	0·80554	0·00693
−10·2	0·74750	0·003239	— 75·4	0·81695	0·008664
−20·2	0·75842	0·003636	— 84·4	0·82621	0·010747
−30·1	0·76906	0·004109	— 92·2	0·83426	0·01334
−32·1	0·77121	0·00420	— 99·8	0·84180	0·01708
−43·0	0·78289	0·00485	−109·8	0·85210	0·02514
−53·9	0·79443	0·00574			

Fig. 2 shows a plot of viscosity against temperature. As in the case of acetone, the curve rises very steeply at the lower tem-

FIG. 2.



peratures. To illustrate further this rapid rate of increase of viscosity, some values of the temperature coefficient have been calculated at each end of the temperature range. These are expressed in Table II as percentage values of the viscosity value at the end of each 10°-interval, *i.e.*, $\alpha = 100(\eta_2 - \eta_1)/\eta_2(T_1 - T_2)$.

TABLE II.

Temperature Coefficients of Viscosity of Ether.

η_1 = viscosity at temp. T_1; η_2 = viscosity at temp. T_2.

T_1.	T_2.	α.	T_1.	T_2.	α.	T_1.	T_2.	α.
0°	−10°	0·99	−40°	−50°	1·33	− 80°	− 90°	2·26
−10	−20	1·10	−50	−60	1·49	− 90	−100	2·72
−20	−30	1·17	−60	−70	1·86	−100	−110	3·24
−30	−40	1·24	−70	−80	1·89			

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XCIV.—*Electrometric Study of the Precipitation of Phosphates.*

By HUBERT THOMAS STANLEY BRITTON.

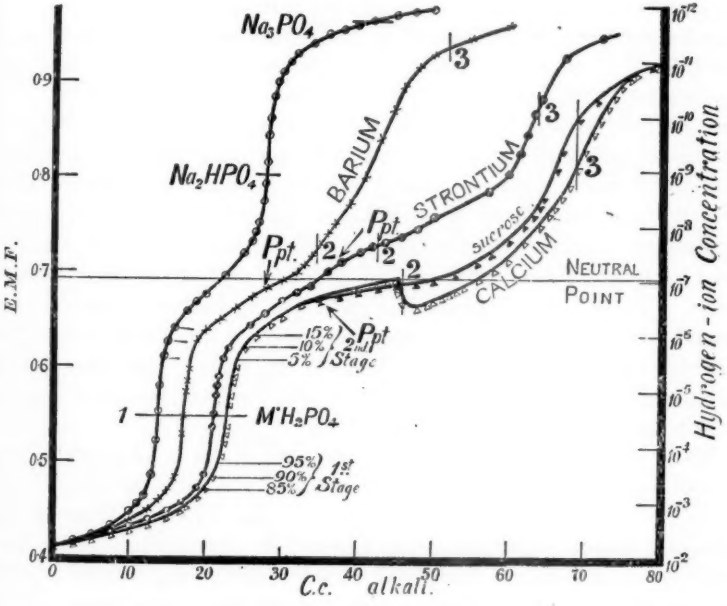
AN attempt is made in this paper to correlate the dissociation of phosphoric acid with the precipitation reactions in which it is involved. Phosphoric acid behaves in its first stage of ionisation as a strong acid, $K_1 = 9{\cdot}4 \times 10^{-3}$, in its second as a weak acid, $K_2 = 1{\cdot}4 \times 10^{-7}$, and in its third stage as an extremely weak acid, $K_3 = 2{\cdot}7 \times 10^{-12}$, so weak that its dissociation can only just be determined. It appears probable, from the very low order of magnitude of K_3, that the third hydrogen atom of phosphoric acid might be incapable of reacting with the majority of weak bases unless the phosphates happen to be very insoluble and the phosphate-ion concentrations of the mother-liquors are kept sufficiently large to exceed the solubility products without permitting the hydrogen-ion concentrations to become so small as to cause precipitation of the hydroxides. Hence, in order to study the part played by phosphoric acid in the various precipitation reactions, the hydrogen-ion concentrations which prevail throughout their courses have been measured by means of the hydrogen electrode. Two series of potentiometric titrations with the hydrogen and normal calomel electrodes have been made in the manner outlined in previous communications (J., 1924, **125**, 1572; 1925, **127**, 2110): the first comprises the reactions between solutions of phosphoric acid and strong bases, *viz.*, the hydroxides of sodium, calcium, barium, and strontium; and the second series deals with the action of trisodium phosphate, chosen because it involves the third stage of ionisation, on solutions of salts of typical metallic bases. A titration by lime water of phosphoric acid in a solution of sucrose was included in the first series in view of the discordant observations of Wendt and Clarke (*J. Amer. Chem. Soc.*, 1923, **45**, 881) and Hoffman and Gortner

(*J. Physical Chem.*, 1925, **29**, 769). [See also Holt, LaMer, and Chown (*J. Biol. Chem.*, 1925, **64**, 509) and Farnell (*J. Soc. Chem. Ind.*, 1926, **45**, 343T).]

Series I.

Fig. 1 gives the hydrogen-electrode titration curves at 20° of (1) 100 c.c. of 0·01277*M*-H_3PO_4 with 0·0919*N*-NaOH, (2) 100 c.c. of 0·00965*M*-H_3PO_4 with 0·0558*N*-$Ba(OH)_2$, (3) 100 c.c. of 0·00765*M*-H_3PO_4 with 0·0359*N*-$Sr(OH)_2$, (4) 100 c.c. of 0·01024*M*-H_3PO_4 with 0·0447*N*-$Ca(OH)_2$, and (5) 100 c.c. of 0·01024*M*-H_3PO_4

FIG. 1.



containing 5 g. of sucrose with 0·0447*N*-$Ca(OH)_2$. With the exception of the sodium hydroxide titration and the alkaline-earth titrations up to the addition of the first equivalent, the *E.M.F.*'s recorded were not true equilibrium values, but were those indicated immediately after each addition of the reactant, for, as Wendt and Clarke observed in their lime-water titrations, the initial *P.D.*'s become smaller when the solutions stand for some time, through the slow reactions which take place between the precipitate and the added alkaline earth.

It is necessary to consider the three dissociation constants of phosphoric acid which have been found to satisfy the sodium hydroxide titration curve, especially in view of the different values

of K_3 which have been reported. Thus Abbott and Bray (*J. Amer. Chem. Soc.*, 1909, **31**, 729) gave K_3 at 18° as $3{\cdot}6 \times 10^{-13}$, whereas Prideaux and Ward (J., 1924, **125**, 423) have recently shown that their p_H measurements and those of other workers give values ranging from 1·54 to $5{\cdot}3 \times 10^{-12}$. Excluding the small portions of the curve about the points of inflexion, the hydrogen-ion concentrations corresponding to the first two sections of the curve are due (see Britton, J., 1925, **127**, 1896) entirely to the equilibria governed by $K_1 = [H^{\cdot}][H_2PO_4']/[H_3PO_4]$ and $K_2 = [H^{\cdot}][HPO_4'']/[H_2PO_4']$, and consequently the simple method adopted in calculating the dissociation constants of malonic acid is applicable. The large hydroxyl-ion concentrations produced during the neutralisation of disodium phosphate with sodium hydroxide are due to a portion of the added alkali taking part in the hydrolysis—in effect remaining unattacked. The concentration of this unattacked alkali may be found directly from the *E.M.F.*'s, assuming the complete ionisation of the solutes, and therefore the concentration of sodium phosphate actually formed is the difference between this and the concentration which would have been produced if all the added alkali had formed trisodium phosphate. The method of calculating K_3 is identical with that previously used to find the dissociation constant of dextrose. Table I gives the *E.M.F.*'s of the hydrogen electrode, compared with the normal calomel electrode, for the titration of phosphoric acid with sodium hydroxide, together with the various calculated ionic concentrations and the dissociation constants to which they lead.

The values of the dissociation constants given in the last column show that the values $K_1 = 9{\cdot}4 \times 10^{-3}$, $K_2 = 1{\cdot}4 \times 10^{-7}$, and $K_3 = 2{\cdot}7 \times 10^{-12}$ reproduce fairly well the three sections of the titration curve. The values of K_1 and K_2 are slightly lower than Abbott and Bray's (*viz.*, $K_1 = 1{\cdot}1 \times 10^{-2}$, $K_2 = 1{\cdot}95 \times 10^{-7}$), whereas that of K_3 is seven times greater than their value. It is, however, in agreement with the recent value of Prideaux.

On comparing the alkaline-earth titration curves, up to the points corresponding to the beginning of precipitation, with that of sodium hydroxide, it will be seen that they cover almost identical ranges of hydrogen-ion concentration. In the lime-water titration precipitation was delayed until 1·53 equivs. (= 35 c.c.) had been added and p_H 6·72 was attained. On standing over-night, a solution of the same concentrations deposited an appreciable amount of precipitate and its p_H fell to 5·98; in fact, precipitates were formed when solutions were allowed to stand which contained only just over 1 equiv. of calcium hydroxide. The delay in precipitation and the high initial p_H were caused by neutralisation taking place

TABLE I.

Titration of 100 c.c. of 0·01277*M*-H_3PO_4 with 0·0919*N*-NaOH at 20°.

(NaH_2PO_4 = 13·9 c.c.; Na_2HPO_4 = 27·8 c.c.)

NaOH (c.c.).	*E.M.F.*	p_H.	$[H_2PO_4']\times10^3$.	$[H_3PO_4]\times10^3$.	$K_1\times10^3$.
0·0	0·408	2·14	7·24	5·53	9·55
2·55	0·416	2·28	7·54	4·92	8·13
5·0	0·423	2·40	8·36	3·80	8·71
7·5	0·433	2·57	9·10	2·78	8·91
10·0	0·447	2·81	9·90	1·71	9·12
11·0	0·455	2·94	10·26	1·24	9·55
12·0	0·464	3·10	10·64	0·76	11·22
13·0	0·486	3·48	10·90	0·36	10·00
13·5	0·521	4·10	11·00	0·26	3·31
				Mean	9·4

NaOH (c.c.).	*E.M.F.*	p_H.	C.c. NaH_2PO_4.	C.c. Na_2HPO_4.	$K_2\times10^7$.
14·5	0·610	5·60	13·3	0·6	1·12
15·0	0·625	5·86	12·8	1·1	1·18
16·0	0·640	6·11	11·8	2·1	1·38
17·5	0·657	6·40	10·3	3·6	1·38
20·0	0·675	6·71	7·8	6·1	1·51
22·5	0·695	7·06	5·3	8·6	1·41
25·0	0·719	7·47	2·8	11·1	1·35
26·0	0·731	7·67	1·8	12·1	1·44
27·0	0·751	8·01	0·8	13·1	1·35
27·5	0·773	8·39	0·3	13·6	1·82
				Mean	1·4

NaOH (c.c.).	*E.M.F.*	p_H.	$[PO_4''']\times10^3$.	$[HPO_4'']\times10^3$.	$K_3\times10^{12}$.
29·0	0·883	10·28	0·66	9·24	3·72
30·0	0·909	10·72	1·02	8·80	2·24
31·0	0·921	10·92	1·42	8·33	2·04
32·0	0·928	11·05	1·80	7·87	2·04
34·0	0·940	11·26	2·43	7·10	1·91
36·0	0·949	11·40	3·03	6·36	1·91
38·0	0·954	11·49	3·70	5·55	2·19
40·0	0·959	11·57	4·29	4·83	2·40
42·5	0·964	11·66	4·91	4·05	2·63
45·0	0·968	11·72	5·65	3·16	3·39
47·5	0·973	11·81	5·81	2·85	3·16
50·0	0·975	11·85	6·52	1·99	4·57
				Mean	2·7

immediately, whereas the precipitation from the supersaturated solution was a matter of time. Had neutralisation only taken place, the hydrogen-ion concentration would have been equal to $[H_2PO_4'] \times K_2/[HPO_4''] = (2 - n) \times 1{\cdot}4 \times 10^{-7}/(n - 1)$, where n is the number of equivs. of alkaline earth, from which it follows that the p_H of the calcium solution when on the point of precipitation should have been 6·91, which is slightly higher than the observed value, 6·72, the difference evidently being due to the precipitation reaction having proceeded to a small extent. The presence of sucrose in the phosphoric acid solution did not impede precipitation. In the baryta titration, 1·62 equivs. were required to start precipitation, which took place at p_H 6·88; on standing over-night further

precipitation occurred and the p_H of the solution fell to 6·07. Strontium hydroxide solution produced a precipitate with 1·78 equivs. (38 c.c.); the p_H was then 7·34, but it became 6·60 after standing over-night, more precipitate having separated. These titrations up to the point of precipitation consisted chiefly of neutralisation, for by calculation it is found that for neutralisation alone the p_H should have been 7·07 in the barium titration instead of 6·88 observed, and 7·40 in the strontium titration instead of 7·34.

The precipitates first formed were the monohydrogen phosphates, $M''HPO_4$, which by the addition of more alkaline earth became converted into the normal phosphates, $M_3(PO_4)_2$. The inflexion in the baryta-titration curve occurred during the addition of the third equiv., and therefore the precipitate was a mixture of di- and tribarium phosphates, whereas in the strontia curve the inflexion was not produced until the third equiv. had been added, showing that the precipitate was the normal strontium phosphate. The final inflexion in the calcium hydroxide titration occurred when the third equiv. had been added, suggesting that at that stage the precipitate was tricalcium phosphate. It will, however, be observed that further additions of lime water did not cause as great an increase in p_H as in the other titrations. This was due to the absorption by the calcium phosphate of some calcium hydroxide thus rendering the phosphate basic. Bassett (J., 1917, **111**, 620) found that one molecule of tricalcium phosphate can absorb one-third of a molecule of calcium hydroxide to form "hydroxyapatite," $3Ca_3(PO_4)_2,Ca(OH)_2$; he believes that this is the calcium phosphate which can permanently exist in the soil under ordinary conditions.

The variation in hydrogen-ion concentration, which occurred in the lime-water reaction just after two equivs. had been added, is remarkable in that the addition of more reactant actually caused an increase in the concentration of hydrogen ions. Wendt and Clarke (*loc. cit.*) found a similar change, but theirs occurred while the second equiv. was being added, doubtless owing to longer times being allowed to elapse before making measurements. An examination of the p_H data corresponding to the addition of the second equiv. of calcium hydroxide in the present titration reveals that the high p_H values were such as would be produced by a large concentration of HPO_4'' ions, caused through supersaturation, as compared with that of H_2PO_4' ions. Assuming that in the first place only the dicalcium phosphate was being formed and partly precipitated, it appears that, when the second equiv. of lime water had been added, the concentration of monocalcium phosphate, and therefore of H_2PO_4' ions, had been reduced to a minimum, the little remaining being produced by the hydrolysis of the precipitate. A sudden diminution

in the concentration of HPO_4'' ions would lead to a sudden increase in p_H. Actually a sudden decrease in p_H was obtained and this was accompanied by further precipitation. It appears probable therefore that the added calcium hydroxide reacted with the dicalcium phosphate remaining in solution, causing precipitation of the tricalcium salt, and in so doing it also decomposed the supersaturated solution, precipitating some dicalcium salt and possibly a little of the normal salt in accordance with the equation suggested by Wendt and Clarke : $4CaHPO_4 = Ca_3(PO_4)_2 + Ca(H_2PO_4)_2$. The p_H data calculated from the phase-rule data of Bassett (*vide infra*) show that both the di- and the tri-calcium phosphates attain equilibrium with liquid phases whose p_H's are about 5·5 through equilibria involving H_2PO_4' and HPO_4'' ions, the former being in considerable excess. It would be expected, therefore, that a p_H of 5·5 would represent the lowest value to which this downward inflexion could attain, and it is interesting to find that this is about the value shown by Wendt and Clarke's curve. The higher p_H obtained by the author is due to insufficient time being allowed for the attainment of final equilibrium. The earlier appearance of the inflexion in Wendt and Clarke's curve was due to the precipitation of the two phosphates of calcium.

Since this work was completed, Holt, LaMer, and Chown (*loc. cit.*), and Farnell (*loc. cit.*) have described similar increases in hydrogen-ion concentration, whereas Hoffman and Gortner (*loc. cit.*), using a solution of calcium sucrate in order to obtain a calcium solution more concentrated than saturated lime water, found no such variation. They considered that the quantity of sucrose present in their work was such as to be without effect on the hydrogen-ion concentrations. The titration curve of phosphoric acid in presence of sucrose given in Fig. 1 shows that sucrose acts as a buffer in preventing an increase in hydrogen-ion concentration. Wendt and Clarke found, by allowing 10 days for the attainment of equilibrium, that the curve became rectilinear during the addition of the greater part of the second and third equivs. of calcium hydroxide, and indicated hydrogen-ion concentrations varying from p_H 5·5, when a little more than the first equiv. had been added, to p_H 6·0 at 2·5 equivs. This is as would be expected from a consideration of Bassett's work (*vide infra*). Farnell obtained similar results by boiling the solutions and cooling to 20° before measuring the p_H. By allowing the solutions to stand over-night in stoppered bottles, the author found that the change in hydrogen-ion concentration was gradual and varied from p_H 5·98 at 1·53 equivs. to p_H 6·52 at 2·5 equivs. These precipitations had not, however, become complete.

The considerable amount of supersaturation, with its consequent effect on the hydrogen-ion concentration, which occurs when alkaline

earths are added to phosphoric acid solutions, renders it difficult to ascertain, by a titration method, when a precipitate should begin to separate. The p_H at which calcium begins to separate as a phosphate is of some importance in the chemistry of soils, and therefore certain data relating to the ternary system CaO–P_2O_5–H_2O obtained by Bassett (J., 1917, **111**, 624; *Z. anorg. Chem.*, 1908, **59**, 1) at 25° and by Cameron and Bell (*J. Amer. Chem. Soc.*, 1905, **27**, 1512) have been studied with respect to the stage of neutralisation of the phosphoric acid in the liquid phases; then, either by comparison with the neutralisation curve (Fig. 1), or by calculation,* an approximate estimate has been made of the hydrogen-ion concentrations of the liquid phases in equilibrium with solid phases containing varying amounts of phosphate. Table II was compiled from Bassett's data, the product $[Ca^{\cdot\cdot}][HPO_4'']$ having been calculated on the assumption that both the mono- and the di-calcium phosphate in solution were completely ionised, an assumption which probably only holds for the very dilute solutions, but which, nevertheless, permits of a satisfactory computation for other solutions. The ionic products $[Ca^{\cdot\cdot}]^3[PO_4'''']^2$ are approximate and were calculated from the hydrogen-ion concentrations, the concentration of HPO_4'' ions, and $K_3 = 2{\cdot}7 \times 10^{-12}$.

It will be seen from the table that those liquid phases which contained 0·149% P_2O_5 (= 0·02*M*-H_3PO_4) or less, as a rule contained calcium hydroxide sufficient to neutralise about 5% of the second stage, giving hydrogen-ion concentrations of the order of $10^{-5{\cdot}5}$. The amount of lime became in excess of 2 equivs. for liquid phases containing less than 0·00613% P_2O_5 (= 0·0009*M*-H_3PO_4). The solid phases which were more basic than $CaHPO_4$ are indicated by the molar ratio PO_4/CaO, which is 0·67 for tricalcium phosphate and 0·60 for the substance, hydroxyapatite, $3Ca_3(PO_4)_2,Ca(OH)_2$. The values of the ratio suggest that the solid phases in equilibrium with the most dilute liquid phases were hydroxyapatite, whereas the ratios corresponding to the more concentrated liquid phases fall, with one exception, between 0·66 and 0·95, proving that the solid phases were either mixtures of tri- and di-calcium phosphate, or possibly dicalcium phosphate in various stages of decomposition. The presence of two solid phases *in equilibrium* with variable liquid phases is incompatible with the phase rule, and it is considered that the conversion of dicalcium phosphate into the normal salt is very slow owing to the ionic requirements of the one being set up simultaneously with those of the other. Consequently, the solid phases may have been indefinite

* The calculation was based on $[H^{\cdot}] = (100 - x) \times 1{\cdot}4 \times 10^{-7}/x$, where x = the % of neutralisation of the second stage, K_2 being assumed to be the same at 25° as at 20°.

TABLE II.

Analysis of Bassett's data of the system $CaO–P_2O_5–H_2O$.

%CaO.	$\%P_2O_5$.	Solid phase.	% Neutralised.*		p_H.	$[Ca^{..}][HPO_4^{''}]$ × 10^6.	$[Ca^{..}]^3[PO_4^{'''}]^2$ × 10^{25}.
1·181	3·613	$CaHPO_4$.	83	(I)	3 apprx.	—	—
0·826	2·387	,,	81	(I)	3 ,,	—	—
0·165	0·417	$CaHPO_4$ and $CaHPO_4,2H_2O$.	0·04	(II)	—	5·9	—
0·0696	0·178	$CaHPO_4,2H_2O$.	99·6	(I)	—	—	—
0·0617	0·149	,,	5·1	(II)	5·6	11·7	13
0·0507	0·121	,,	6·3	(II)	5·7	9·7	16
0·0485	0·119	,,	3·3	(II)	5·4	4·9	1·0
0·0427	0·105	,,	3·1	(II)	5·4	3·5	0·4
		PO_4/CaO in solid phase.					
0·0406	0·0980	0·76	5·1	(II)	5·6	5·1	2·0
0·0389	0·0947	0·79	4·1	(II)	5·5	3·8	0·8
0·0373	0·0897	0·95	5·5	(II)	5·6	4·6	1·6
0·0326	0·0777	0·62	6·4	(II)	5·7	4·1	1·6
0·0299	0·0727	0·67	4·4	(II)	5·5	2·4	0·2
0·0269	0·0607	0·66	12·4	(II)	6·0	5·1	7·9
0·0191	0·0465	0·70	4·1	(II)	5·5	0·9	0·02
0·0175	0·0423	0·71	4·9	(II)	5·6	0·9	0·05
0·0174	0·0414	0·69	6·5	(II)	5·7	1·2	0·08
0·0167	0·0405	0·69	4·6	(II)	5·5	0·8	0·01
0·0126	0·0332	—	96	(I)	—	—	—
0·0122	0·0302	0·66	2·4	(II)	5·2	0·2	0·0003
0·00893	0·0196	0·63	12·0	(II)	6·0	0·4	0·03
0·00582	0·0134	0·62	10·1	(II)	5·9	0·2	0·002
0·00600	0·00613	0·62	4·9	(III)	11 apprx.	—	—

* The Roman numerals (I), (II), and (III) relate to the first, second, and third stages, respectively.

and unstable mixtures, although it appeared, as far as could be ascertained experimentally, that equilibrium had been established. The foregoing explanation appears to be valid, for if the solubility product of dicalcium phosphate be assumed to be 5×10^{-6} (approx.), and that of the tricalcium salts to be about 1×10^{-25}, then it is evident from the table that for many liquid phases the two stipulated conditions prevailed at the same time. The decrease in the ionic product of the tricalcium salt (shown by the last few values in the last column) to less than the probable value of the solubility product, 1×10^{-25}, may have been due to the formation of a basic phosphate.

The p_H data given in Table II are of interest on account of their bearing on the reactions which take place in soils when treated with phosphatic fertilisers. If the p_H of the "soil solution" falls below 5·5, the calcium phosphate in the soil will pass into the soluble state, though when in this condition there will be a great tendency for some of the phosphate to suffer "reversion" through reaction with colloidal alumina, but when lime is added so as to raise the p_H to 5·5 and above, the phosphate begins to become insoluble, initially as the dicalcium salt, and finally as the basic phosphate. It would appear

that these changes in the composition of the insoluble calcium phosphate can take place without any great diminution in the acidity of the soil. The p_H, 5·9, attained when the PO_4/CaO ratio in the solid phases had become 0·62, confirms Bassett's observation that hydroxyapatite can exist in faintly acid as well as in neutral or alkaline solutions, and that it can probably exist permanently in soils under ordinary conditions, for any di- or tri-calcium phosphate which may first be formed will ultimately become decomposed.

Soil solutions in equilibrium with the dicalcium phosphate contain relatively large amounts of partly neutralised phosphoric acid which, when removed either by "reversion," by the plant, or by drainage, will cause the solid phases to decompose and eventually to become basic without any great change in p_H taking place. The conversion of the phosphate into the insoluble basic state renders it unavailable to the plant. Thus Gedroiz (*Zhur. Opit. Agron.*, 1911, **12**, 529) found that tricalcium phosphate gave the best immediate results on soils not saturated with bases. The necessity of having the soil just on the acidic side of neutrality has recently been emphasised by von Wrangell (*Landw. Vers.-Stat.*, 1920, **96**, 1), who recommends the use of "physiologically acid fertilisers," such as ammonium sulphate, to render any phosphate available.

Series II.

The variation in hydrogen-ion concentration which occurred at 20° when a $N/10$-solution of trisodium phosphate was added to 100 c.c. of the salt solutions (Table III) was followed electrometrically. The *E.M.F.*'s were reproducible, except in the final stages of the chromium and magnesium titrations. Table III also contains the p_H's at which the phosphate precipitates began to separate, and, for purposes of comparison, the respective hydroxide p_H's.

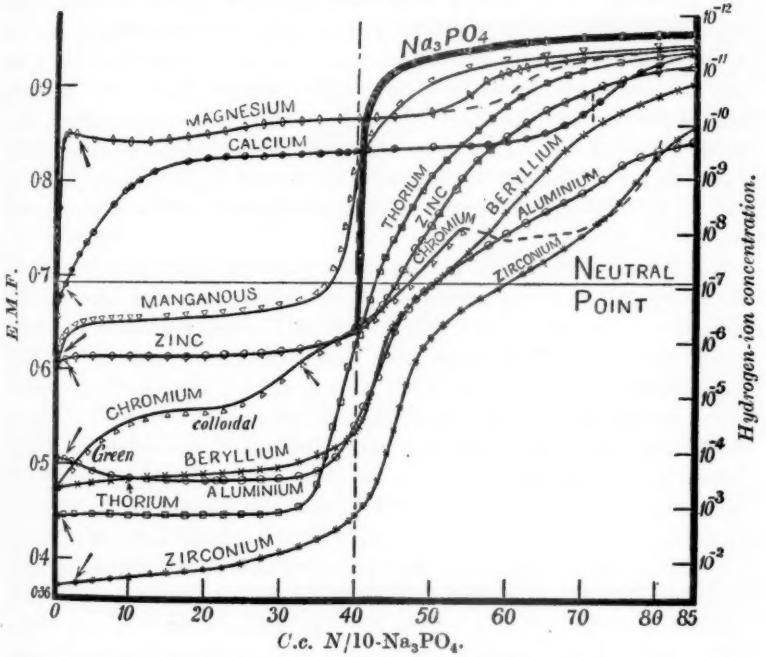
TABLE III.

Solution titrated.	Phosphate p_H.	Hydroxide p_H.
0·02*M*-$MgSO_4$	9·76	10·49
0·0358*M*-$CaCl_2$	7·00	—
0·02*M*-$MnCl_2$	5·76	8·43
0·02*M*-$ZnSO_4$	5·66	5·20
0·00667*M*-$Cr_2(SO_4)_3$,K_2SO_4	{4·62 / 5·65}	5·34
0·00667*M*-$Al_2(SO_4)_3$	3·79	4·14
0·02*M*-$BeSO_4$	3·41	5·69
0·01*M*-$ThCl_4$	2·72	3·51
0·01*M*-$ZrCl_4$	1·57	1·86

The curves showing the hydrogen-ion concentrations acquired when increasing amounts of trisodium phosphate had been added are given in Fig. 2. The amount of trisodium phosphate required

to form the normal metallic phosphate was 40 c.c. in every case except that of calcium chloride, in which it was 71·6 c.c. The curve marked Na_3PO_4 was obtained by adding $N/10$-sodium phosphate solution to 140 c.c. of solution (*i.e.*, the volume attained in the precipitation reactions when stoicheiometrical amounts of the phosphate solution had been added) containing an amount of sodium chloride equal to the amount of neutral salt formed in the precipitation reactions with 40 c.c. of sodium phosphate. It would therefore represent the variation in hydrogen-ion concentration on

FIG. 2.



adding an excess of the reactant, if the pure normal phosphates had been precipitated, leaving in solution amounts of phosphate so small as to exert no " buffer action." The arrows denote the beginning of precipitation.

In no instance did the curve corresponding to an excess of the reactant coincide with this curve, the two nearest being those of manganese and calcium. The others are widely divergent. The p_H data given in Table III show that the phosphate precipitates, with the exception of that of zinc, separated from solutions whose hydrogen-ion concentrations were greater than those requisite for the precipitation of the corresponding hydroxides; and thus it

appears that, whilst it may be possible to obtain the normal phosphates by the use of an amount of trisodium phosphate insufficient to give complete precipitation, yet as soon as sufficient reactant has been added to bring the p_H of the solution to that necessary for the precipitation of the hydroxide, any metallic salt remaining in solution will then be precipitated, and, moreover, there will be a strong tendency for the precipitate to be decomposed. That some such reaction must have taken place is evident from the curves. The depression of the manganese and the calcium curves must have been caused by the " buffer action " of the added sodium phosphate on the HPO_4'' ions, which had been supplied to the solutions by the precipitates. The greater hydrogen-ion concentrations set up in the zinc, beryllium, aluminium, and thorium reactions were, as may be seen from the sodium hydroxide curve in Fig. 1, of the same magnitude as those produced in the second, and subsequently the third, stage of neutralisation. Hence the precipitates must have decomposed to furnish the mother-liquor with H_2PO_4' ions, some of which, by reacting with the added phosphate, became converted into HPO_4'' ions.

No inflexion occurred in the zirconium chloride reaction when the stoicheiometrical quantity of sodium phosphate had been added, though one appeared on the addition of a small excess. By comparing the range of hydrogen-ion concentrations produced during the addition of this excess with that obtained towards the end of the neutralisation of the first stage of phosphoric acid (Fig. 1), it will be seen that the equilibria which produce these relatively large concentrations of hydrogen ions involve some free phosphoric acid. This must have been liberated through the extreme weakness of zirconium hydroxide, with the result that a highly basic zirconium phosphate was precipitated, the formation of which might have been inferred from the fact that zirconium chloride solutions are very considerably hydrolysed. Thus it was found (Britton, J., 1925, **127**, 2133) that a freshly prepared solution of the concentration used in this titration was hydrolysed to the extent of 54%, and consequently the free acid liberated an equivalent amount of phosphoric acid on reacting with trisodium phosphate. The middle point of the first inflexion (corresponding with the addition of 45 c.c., an excess of 5 c.c.) represents the stage when the liberated phosphoric acid had reacted with the added phosphate to form monosodium phosphate, in accordance with the equation $Na_3PO_4 + 2H_3PO_4 = 3NaH_2PO_4$, from which it follows that the excess of 5 c.c. reacted with twice the amount, *i.e.*, 10 c.c., of phosphoric acid. The total amount of phosphoric acid was equivalent to 40 c.c., and of this 13·3 c.c. corresponded to the first stage of dissociation. The

amount of phosphoric acid which had escaped precipitation was therefore 10/13·3 of the quantity required for the normal phosphate of zirconium, and hence the composition of the precipitate might be represented as $6ZrO_2,P_2O_5$. The curve obtained on adding a further excess of the reactant, instead of being sharply inflected through p_H 9 owing to the complete formation of disodium phosphate, showed that a considerable "buffer action" occurred between p_H 6 and 10. It appears, therefore, from the expression $[H^\cdot] = K_2[H_2PO_4']/[HPO_4'']$ governing the hydrion concentrations during the second stage of neutralisation, that the precipitate itself, in being decomposed, must have exerted some buffering action by imparting to the mother-liquor a small but continuous concentration of H_2PO_4' ions.

The precipitation curve of aluminium phosphate is interesting in that the first addition of sodium phosphate caused an increase in the concentration of hydrogen ions, reaching a maximum at p_H 3·43 with 17·5—20 c.c. The precipitate became very basic when an excess of sodium phosphate was added as shown by the comparatively large buffering effect—at 80 c.c. the p_H was 9·41; at 100 c.c., 10·02; at 120 c.c., 10·24; and at 140 c.c., 10·33. The hydrolysis of the precipitate into aluminium hydroxide was accompanied by its gradual dissolution in the sodium phosphate solution. Thus the solution became translucent with 80 c.c. and quite clear with 140 c.c. Reference to the hydrogen-ion concentration curve showing the action of alkali on aluminium sulphate solution (Britton, J., 1925, **127**, 2121) shows that sodium aluminate began to form when the p_H became between 9 and 10. Hence it appears that the dissolution of the precipitate in an excess of sodium phosphate was due to the formation of sodium aluminate, the necessary free alkali being furnished by the trisodium phosphate through the exceptional weakness of phosphoric acid in its third stage of ionisation and the resulting hydrolysis of its sodium salt. The inability of disodium phosphate, when added in excess, to cause the precipitate to dissolve is due to the low p_H which it sets up. An excess of this precipitant reduces the hydrogen-ion concentration considerably below that at which aluminium hydroxide becomes precipitable, causing the precipitate to hydrolyse. Thus Munroe (*Amer. J. Sci.*, 1871, [iii], **1**, 329) found that a precipitate, $AlPO_4,Al(OH)_3,2{\cdot}5H_2O$, was obtained when an alum solution was treated with an excess of the disodium salt.

The ease with which aluminium phosphate becomes decomposed on decreasing the hydrogen-ion concentration, even though the reagent used may itself be a soluble phosphate, throws some light on the manner in which vegetation obtains its phosphorus from

the soil. When a soluble phosphatic fertiliser, such as superphosphate of lime, is added to a soil, and especially if the soil be sour, " reversion " of the phosphate occurs through the formation of insoluble phosphate on the surfaces of the colloidal particles of hydrated alumina and ferric oxide (see, *e.g.*, Lichtenwalner, Flenner, and Gordon, *Soil Sci.*, 1923, **15**, 157; Hall and Vogel, *ibid.*, p. 367). Marais (*ibid.*, 1922, **13**, 355), in a study of the application of aluminium phosphate as a fertiliser, concluded that, in spite of its low solubility in citric acid, it is of service in soils well stocked with lime, but should never be used on acid soils unless lime is applied in intimate contact with it. Slaked lime causes aluminium phosphate to decompose with the formation of soluble calcium phosphate until p_H 5·5 is reached.

In the author's earlier papers, stress was laid on the remarkable property of beryllium and chromium in forming " soluble basic salts," and attempts have been made to trace any effects that this factor may have on the reactions of the salts of these metals. Precipitation of the basic chromate, carbonate, and borate did not occur until comparatively large amounts of precipitant had been added, and considerable changes in hydrogen-ion concentration had taken place (J., 1925, **127**, 2120; 1926, 125). Although precipitation did not take place from the beryllium sulphate solution until 7·5 c.c. of sodium phosphate had been added, the delay was not accompanied by any great change in hydrogen-ion concentration. As mentioned above, the beryllium precipitate was a basic phosphate. Bleyer and Müller (*Z. anorg. Chem.*, 1913, **79**, 263) assigned the formula $BeO,2Be_3(PO_4)_2,13H_2O$ to a precipitate similarly obtained.

In the chromium sulphate titration, however, the effect was pronounced. At first the sodium phosphate merely caused the violet solution to turn green—a point of importance in connexion with the question of the colours of chromium salt solutions, and one which has always been observed whenever a violet chromium salt solution has been rendered basic (*loc. cit.*). Simultaneously an appreciable decrease in hydrogen-ion concentration occurred until 12 c.c. (= 0·90 equiv. per atom of Cr) had been added, $p_H = 4·62$, a cloudiness then being observed. For the next 10 c.c. the p_H remained nearly constant, although the solution became more and more colloidal, and thereafter a steady rise in p_H occurred, coagulation taking place at p_H 5·65 with 32·5 c.c. (= 2·44 equivs.). The bulk of the precipitate was green and flocculent, but it contained a small quantity of a violet crystalline precipitate, apparently the normal chromium phosphate. The delay in precipitation is significant, as also is the fact that when it took place the hydrogen-ion concentration of the mother-liquor was not very far from that

at which chromium hydroxide is precipitated, *viz.*, p_H 5·3. The diminution in hydrogen-ion concentration was gradual until 54 c.c. (= 4·05 equivs.) of sodium phosphate had been added, $p_H = 8·07$, at which stage the *E.M.F.*'s not only became very unsteady, but also showed a remarkable increase in hydrogen-ion concentration. The changes which took place immediately after the addition of each new amount of sodium phosphate are shown by the broken line. The hydrogen-ion concentration subsequently grew smaller, such that when 80 c.c. had been added the p_H had become 9·71. Precipitation became complete just after the stoicheiometrical amount of sodium phosphate, 40 c.c., had been added. The change in p_H with the excess of reactant shows that a basic phosphate had been precipitated, and the exceptional change after 4 equivs. of sodium phosphate had been added indicates that the precipitate underwent rapid hydrolysis. The p_H, 8·07, attained when this change began was that which would have been produced by a solution of phosphoric acid neutralised by caustic soda almost to Na_2HPO_4, *i.e.*, in the present reaction, according to the equation $2Na_3PO_4 + H_3PO_4 = 3Na_2HPO_4$. Hence the equivalent which was in excess of the amount necessary to form the normal chromium phosphate required approximately one-sixth of a molecule of phosphoric acid to bring the p_H of the solution up to about 8, and therefore the amount of phosphoric acid in combination with the precipitate at that stage was about five-sixths of that present in the normal phosphate. It has been suggested (J., 1925, **127**, 2120) that in the ordinary violet chromium salts approximately one equiv. of acid radical exists in a looser kind of combination than do the other two equivs., so that chromium sulphate in solution might be represented as $Cr_2(SO_4)_2(OH)_2$---H_2SO_4, and therefore on treatment with trisodium phosphate the first reaction to take place would be the replacement of this loosely bound molecule of sulphuric acid by two-thirds of a molecule of phosphoric acid, and unless the solubility-product requirements of the normal chromium phosphate are simultaneously satisfied no precipitation would ensue, although a change in hydrogen-ion concentration would be produced, comparable with that set up in the reactions of chromium salts which involve the precipitation of basic salts.

The p_H, 5·66, at which the zinc phosphate precipitate began to form was a little higher than that required by zinc hydroxide, *i.e.*, 5·20, but reference to the hydroxide precipitation curve (Britton, J., 1925, **127**, 2125) shows that the p_H during the main part of the precipitation was 6, whereas the phosphate curve shows a slightly lower p_H, *viz.*, 5·7.

The *E.M.F.*'s recorded in the reaction with calcium chloride up to

the addition of 7 c.c. of sodium phosphate tended to be low initially but slowly increased to steady values; for larger volumes of sodium phosphate the voltages given primarily appeared to be reproducible. The stoicheiometrical amount of sodium phosphate was 71·6 c.c., and this, as seen from the curve, gave rise to a hydrogen-ion concentration which was represented by a point of the inflexion corresponding to the completion of precipitation as the normal calcium phosphate. The greater part of the precipitation occurred between p_H 9·5 and 10 and, as will be seen from the sodium hydroxide titration curve (Fig. 1), such a p_H corresponds to equilibria involving a predominance of HPO_4'' and very few PO_4''' ions, thus $HPO_4'' + OH' \rightleftharpoons PO_4''' + H_2O$, which must have been given by the hydrolysis of the tricalcium phosphate into the dicalcium salt: $Ca_3(PO_4)_2 + 2H_2O = 2CaHPO_4 + Ca(OH)_2$. The difference between the p_H's which prevailed during the precipitation of calcium phosphate in series I and II was due to suppression of the hydrolysis in the former case by the presence of a small amount of partly neutralised phosphoric acid, whereas this was absent in the double decomposition. There is, however, very little difference in the p_H's of precipitation of the phosphates of the weaker base-forming metals, *e.g.*, zinc and cobalt.

The precipitation from the magnesium sulphate solution is of interest for two reasons. First, the inflexion indicating the end of precipitation did not appear when the stoicheiometrical amount of sodium phosphate had been added, *viz.*, 40 c.c., but occurred with about $1\frac{1}{2}$ times that quantity. Secondly, the solution from which the precipitate had separated was even more alkaline than that in the calcium reaction, the p_H at which the precipitate began to form being 9·76. The exact incidence of the inflected part depended on the efficiency of agitation of the reaction mixture and on the time allowed before measuring the *E.M.F.* The broken line was obtained by allowing longer time, and the inflexion began at 60 c.c., whereas the first curve was undergoing inflexion with that amount. A p_H of 9·76 must have been produced by the same kind of ionic equilibria as in the calcium phosphate precipitation, in which, however, there was a greater proportion of phosphate ions. The amount of sodium phosphate required to effect precipitation suggests the reaction $MgSO_4 + Na_3PO_4 = MgHPO_4 + NaOH + Na_2SO_4$, but the fact that the p_H remained almost stationary at 10 throughout the course of precipitation shows that the concentration of free alkali was relatively small. Analyses of the mother-liquors showed that the sodium hydroxide had combined with the precipitated magnesium phosphate in the form of a double phosphate, $MgNaPO_4$, and it was therefore the hydrolysis of this double phosphate into magnesium

hydrogen phosphate and sodium hydroxide which determined the p_H throughout the precipitation.

Note on the Phosphate Separation.

The observations made in the course of these electrometric titrations afford a satisfactory explanation of the procedure adopted in qualitative analysis for the removal of phosphates. The phosphate precipitation p_H's are functions of the concentrations of both the metallic and the phosphate ions, and the use of dilute solutions tends to keep the concentrations of both the bases and phosphoric acid comparatively small, and thereby fixes within narrow limits the p_H at which the various phosphates are precipitated as the free acid is gradually neutralised and the solution made alkaline. The hydrogen-ion concentrations which prevailed during the formation of the phosphate precipitates (Fig. 2) are approximately those which would be set up if the phosphoric acid had been present in the solution and was subsequently neutralised with alkali. In the "basic acetate" method of removing phosphates, the solution, before treatment with ferric chloride solution, is buffered at about p_H 5 by the acetic acid and an excess of either sodium or ammonium acetate. Fig. 2 shows that the only phosphates to be precipitated from solutions more acid than p_H 5 are those of zirconium, thorium, aluminium, beryllium, and chromium. Ferric phosphate is also precipitated from very acid solutions. The phosphates and hydroxides which are precipitated from solutions of p_H higher than 5 are those of zinc, manganese, calcium, and magnesium, to which should be added cobalt, nickel, strontium, barium, and many of the rare earths. It appears, therefore, that as the p_H of the phosphate solution is raised to 5, the phosphates precipitated will be, first, ferric, then aluminium, and finally chromium, but if the quantity of phosphoric acid in the solution is inadequate to form any or all of these phosphates, then the acid will combine with the bases in the order in which they are precipitated, and consequently the hydroxides themselves may be precipitated. Hence, by having a quantity of these three bases, and preferably of ferric hydroxide, more than sufficient to combine with the total amount of phosphoric acid present, the phosphate will be completely removed without precipitation of the bases belonging to the subsequent groups. Acetic acid has a marked tendency, owing to the formation of soluble basic acetates, to retain the hydroxides in solution even though the p_H's at which they are normally precipitated may have been exceeded (*vide* Britton, J., 1926, 269). These acetate solutions are, however, completely decomposed on boiling, although long boiling may be necessary if too much acetate be used.

Summary.

(1) The dissociation constants, $K_1 = 0{\cdot}94 \times 10^{-2}$, $K_2 = 1{\cdot}4 \times 10^{-7}$, and $K_3 = 2{\cdot}7 \times 10^{-12}$, at 20°, have been shown to satisfy the hydrogen-electrode titration curve of phosphoric acid by sodium hydroxide.

(2) The hydrogen-electrode curves of phosphoric acid in course of neutralisation by the alkaline earths show that this process at first goes beyond the limits fixed by the very small solubilities of the alkaline-earth phosphates, which later become precipitated, although a considerable time must elapse before equilibrium between the precipitates and the solutions is established.

(3) The presence of sucrose in a phosphoric acid solution prevents the exceptional increase in hydrogen-ion concentration which ordinarily occurs during precipitation with calcium hydroxide.

(4) Calculations from Bassett's data for the system CaO–P_2O_5–H_2O at 25° show that calcium phosphate is not precipitated from solutions which are more acid than p_H 5·5. Probable values for the solubility products of di- and tri-calcium phosphates have been found.

(5) Hydrogen-electrode titrations with trisodium phosphate of salt solutions of zirconium, thorium, aluminium, beryllium, chromium, zinc, manganese, magnesium, and calcium have been described, in which it has been shown that all, except the last two, yield basic phosphates. Magnesium forms a double phosphate with sodium. The redissolution of the aluminium precipitate in an excess of precipitant has been traced to the formation of sodium aluminate.

(6) The importance of the p_H data relating to the precipitation of phosphates has been emphasised in respect of (*a*) the application of phosphatic fertilisers to soils, and (*b*) the removal of phosphates in qualitative analysis.

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XCV.—*The Nitration of* m-*Iodophenol.*

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THE investigation of the direct nitration of *m*-iodophenol proceeded on similar lines to the work on *m*-chloro- and *m*-bromo-phenols (J., 1925, **127**, 1599; 1926, 155). 3-Iodo-2-, -4-, and -6-nitro-

phenols, 3-iodo-4 : 6- and -2 : 6-dinitrophenols, and 3-iodo-2 : 4 : 6-trinitrophenol were prepared, but 3-iodo-2-nitrophenol was obtained from the nitration mixture with difficulty owing to the instability of *m*-iodophenol towards sulphuric acid and oleum and to the tardy mono- but ready tri-nitration of the sulphonic acid produced.

The constitutions of 3-iodo-4- and -6-nitrophenols are determined by analogy with those of the corresponding chloro- and bromo-compounds (*loc. cit.*), by their conversion into 2 : 2′-dinitro- and 4 : 4′-dinitro-5 : 5′-dimethoxydiphenyl disulphides and into 2-nitro- and 4-nitro-5-methoxythioanisoles, respectively (Hodgson and Handley, J., 1926, 543), and also by the conversion of each by nitration into 3-iodo-4 : 6-dinitrophenol, which is converted into 4 : 6-dinitroresorcinol on prolonged boiling with aqueous potassium hydroxide. Since 3-iodo-5-nitrophenol has been described by Hodgson and Wignall (J., 1926, 2077), the constitution assigned to 3-iodo-2-nitrophenol is the only one left for this substance. The constitution of 3-iodo-2 : 6-dinitrophenol follows from its preparation from 3-iodo-2- and -6-nitrophenols, and that of 3-iodo-2 : 4 : 6-trinitrophenol from its formation from all the mono- and both the di-nitro-derivatives.

Owing to the extensive decomposition of *m*-iodophenol by concentrated sulphuric acid and the consequent paucity of 3-iodo-2-nitrophenol, we have been unable to obtain 3-iodo-2 : 4-dinitrophenol. Attempts to substitute an amino-group for the halogen in 3-chloro- or 3-bromo-2-nitrophenol and so provide an alternative method for the preparation of 3-iodo-2-nitrophenol were unsuccessful, although the most drastic conditions were employed. The great stability of the halogen thereby demonstrated is found also in 3-iodo-2-nitrophenol, and in 3-iodo-2 : 4 : 6-trinitrophenol, which readily sublimes from boiling concentrated sulphuric acid. On the other hand, 4 : 6-di-iodo-1 : 3-dinitrobenzene, when boiled with a dilute solution of an alkali hydroxide or carbonate, slowly but completely exchanges the whole of its iodine for hydroxyl.

Unlike the corresponding chloro- and bromo-compounds, 3-iodo-2-nitrophenol does not form a hydrate. This was to be expected, since the hydrate of the chloro-compound is very much more stable than that of the bromo-compound. 2-Chloro-6-nitrophenol also does not appear to form a hydrate. The property, therefore, seems to be peculiar to the 3-chloro- and 3-bromo-2-nitrophenols.

Busch's α- and β-iodonitrophenols (*Ber.*, 1874, **7**, 462), which are stated to be 5- and 6-iodo-2-nitrophenols (Beilstein, " Organische Chemie," II, p. 700), are regarded as impure substances by Roberts (J., 1923, **123**, 2710) and as 3- and 4-iodo-2-nitrophenols by Keimatsu (*J. Pharm. Soc. Japan*, 1924, No. 507, 319). Since all

the monoiodo-2-nitrophenols are now available, one of the authors (H. H. H.) is repeating Busch's work with the object of determining the mechanism of iodination in presence of mercury compounds.

Experimental.

m-Iodophenol was prepared by the general method (Hodgson, E.P. 200714) from diazotised *m*-iodoaniline. It loses iodine in the presence of boiling water.

Mononitration of m-*Iodophenol.*

3-*Iodo*-6- *and* -4-*nitrophenols.*—*m*-Iodophenol (21·3 g.), liquefied by alcohol (2 c.c.), was added slowly to a solution, vigorously stirred at 15°, of concentrated sulphuric acid (22 g.) and sodium nitrate (16 g.) in water (40 c.c.). After 2 hours, the tarry mass was removed, washed, and steam-distilled; some iodine accompanied the volatile product, 3-*iodo*-6-*nitrophenol* (3·7 g.), which crystallised from light petroleum in long, yellow needles, m. p. 96° (Found: N, 5·5; I, 47·7. $C_6H_4O_3NI$ requires N, 5·3; I, 47·9%).

3-Iodo-6-nitrophenol forms a scarlet *sodium* salt and a stable, orange-brown *silver* salt. Its *methyl* ether was obtained by boiling a solution of 1 g. of the phenol in aqueous sodium carbonate (1 g. in 40 c.c. of water) with methyl sulphate (1·5 c.c.) for 5 minutes, and steam-distilling the product. The white solid thus obtained crystallised from dilute alcohol in shining plates, m. p. 92° (Found: I, 45·3. $C_7H_6O_3NI$ requires I, 45·5%). The *acetate* was prepared by warming an excess of acetyl chloride with a solution of 3-iodo-6-nitrophenol in glacial acetic acid for a short time on the water-bath. On diluting the mixture with water and cooling it, 3-*iodo*-6-*nitrophenyl acetate* separated in hexagonal plates which, after recrystallisation from acetic acid containing a little acetic anhydride, melted at 95° (Found: I, 41·1. $C_8H_6O_4NI$ requires I, 41·4%). The *benzoate*, which was prepared in the same way as the corresponding chloro-compound, separated from alcohol in colourless needles, m. p. 122°.

The liquid remaining after the steam distillation of 3-iodo-6-nitrophenol was filtered hot from the tarry matter; on cooling, it deposited 3-iodo-4-nitrophenol as a yellowish-white solid, which crystallised from light petroleum in very pale yellow needles, m. p. 124° (Found: N, 5·4; I, 47·6%). The tar solidified on cooling, and on crystallisation from benzene and light petroleum gave a further quantity of 3-iodo-4-nitrophenol (total yield, 10 g.). The *sodium* salt formed amber-coloured needles; the yellow *silver* salt darkened on keeping. The *methyl* ether, prepared as described

above for the 6-nitro-isomeride, crystallised from dilute alcohol in cream-coloured needles, m. p. 69—70° (Found : I, 45·2%). The *benzoate* separated from alcohol in long, slender, colourless needles, m. p. 119°. The *acetate* separated from dilute acetic acid in fine, colourless needles, m. p. 73·7° (Found : I, 41·2%).

Oxidation of 3-Iodobenzoquinone-4-oxime.—A solution of the oxime (1 g.) in water (200 c.c.) containing sodium hydroxide (10 g.) and potassium ferricyanide (10 g.) was kept for 48 hours at room temperature; the dark red colour had then changed to amber. On acidification with dilute sulphuric acid, the solution became green and deposited a voluminous, white precipitate (0·3 g.); ether extracted from the filtrate a further 0·4 g. The product crystallised from benzene in pale yellow needles, m. p. 123° (Found : N, 5·5%), and was 3-iodo-4-nitrophenol. This result proves that the nitrosation of *m*-iodophenol takes place in the 4-position (see J., 1925, **127**, 2260).

3-Iodo-2-nitrophenol.—*m*-Iodophenol (7·5 g.) was added very gradually to oleum (12 c.c.; 27%), the mixture being cooled after each addition. After 1 hour, the temperature was raised gradually to 70—80° and maintained for 1½ hours. The mixture, which had then become a paste of crystals, was cooled, diluted with concentrated sulphuric acid (10 c.c.), and nitrated with a solution of nitric acid (2·5 c.c.; *d* 1·5) in concentrated sulphuric acid (7·5 c.c.), added at such a rate that the temperature never exceeded 30°. After 2 hours, the whole was poured on ice, and the solution carefully concentrated in a current of steam; iodine was evolved continuously, and from the highly concentrated, extensively decomposed product a yellow oil distilled which was collected in numerous small fractions. The earlier fractions would not solidify and were mixtures of *m*-iodophenol and 3-iodo-2-nitrophenol, but the later ones, on cooling, crystallised in long, yellow needles, m. p. 70—71°. The yield was variable and never exceeded 12%. When the quantity of nitric acid was increased, 3-iodo-2 : 4 : 6-trinitrophenol was the main product with a little 3-iodo-2 : 6-dinitrophenol. Diminution of the quantity of nitric acid resulted in a product which did not solidify and was mainly *m*-iodophenol.

3-Iodo-2-nitrophenol crystallised from water or light petroleum in bright greenish-yellow, spear-shaped needles, m. p. 73·5° (Found : N, 5·3; I, 47·8. $C_6H_4O_3NI$ requires N, 5·3; I, 47·9%). No formation of hydrate could be detected. The *sodium* salt crystallises in orange needles and the *ammonium* salt in red, rectangular plates which readily hydrolyse; the *silver* salt has a deeper orange-brown colour than its 6-nitro-isomeride and rapidly darkens on keeping. The *methyl* ether prepared in the way described above, crystallises

from dilute alcohol in colourless micro-plates, m. p. 82—83° (Found: I, 45·2. $C_7H_6O_3NI$ requires I, 45·5%). The *acetate* separates from dilute acetic acid in colourless cubes, m. p. 102·5° (Found: I, 41·2. $C_8H_6O_4NI$ requires I, 41·4%). Mixed with the 6-nitro-isomeride, it melts at 80°.

Dinitration of m-*Iodophenol.*

3-*Iodo*-4 : 6-*dinitrophenol* was prepared from *m*-iodophenol and from 3-iodo-6- and -4-nitrophenols in the same way as the corresponding bromo-compound (*loc. cit.*, p. 158). It is readily volatile in steam and crystallises from light petroleum in yellowish-white needles and from water in yellowish-white plates, m. p. 98° (Found: N, 9·2; I, 40·7. $C_6H_3O_5N_2I$ requires N, 9·0; I, 40·9%). The *silver* salt formed as a bright yellow, gelatinous precipitate when a neutral solution of the ammonium salt was treated with aqueous silver nitrate; it is moderately easily soluble in ammonia, but readily soluble in boiling water, from which it crystallises in golden needles (Found: Ag, 25·6. $C_6H_2O_5N_2IAg$ requires Ag, 25·9%). The gelatinous form changes to a redder, crystalline variety on keeping.

3-*Iodo*-2 : 6-*dinitrophenol.*—*m*-Iodophenol (5·5 g.) was gradually dissolved in 20 c.c. of oleum (27% SO_3), the mixture being cooled after each addition. After 48 hours, nitration below 0° was effected during 30 minutes with a solution of nitric acid (5 c.c.; *d* 1·5) in oleum (15 c.c.), and 2 hours later the whole was poured on ice, and the deep orange solution steam-distilled. Iodine was evolved and almost at the outset of the distillation the main part of the reaction product, which was 3-iodo-2 : 4 : 6-trinitrophenol, separated and was filtered off. The concentration by steam distillation was then continued, with evolution of iodine, and finally 3-*iodo*-2 : 6-*dinitrophenol* passed over slowly; it separated from the distillate in almost colourless, slender needles which, after recrystallisation from water, dilute acetic acid, or light petroleum, melted at 151—152° (Found: N, 9·2; I, 40·7. $C_6H_3O_5N_2I$ requires N, 9·0; I, 40·9%). 3-Iodo-2 : 6-dinitrophenol is readily turned yellow by ammonia, forms yellow solutions in water and alcohol, and very deep yellow ones with dilute aqueous alkalis. The *silver* salt separates slowly in bright orange-red needles when prepared by the usual method, and is sparingly soluble in ammonia and hot water.

3-Iodo-2 : 6-dinitrophenol was also prepared from 3-iodo-2-nitrophenol and from 3-iodo-6-nitrophenol in the same ways as the corresponding chloro- (*loc. cit.*, p. 1602) and bromo- (*loc. cit.*, p. 159) compounds, respectively.

Trinitration of m-*Iodophenol.*

3-*Iodo*-2 : 4 : 6-*trinitrophenol* was prepared in excellent yield as described above, or by the method used for the preparation of the corresponding chloro-compound (*loc. cit.*, p. 1603). It is not volatile in ordinary or in superheated steam, but sublimes slowly from boiling concentrated sulphuric acid. It crystallises from water, in which it is much less soluble than the corresponding chloro- and bromo-compounds, in almost colourless needles, and from glacial acetic acid in characteristic parallelepipeds, m. p. 197° (Found : N, 11·6; I, 35·5. $C_6H_2O_7N_3I$ requires N, 11·8; I, 35·8%). The substance possesses pronounced sternutatory properties, forms deep yellow solutions in water and alcohol, and is not brominated when its solutions are treated with bromine. The yellow *silver* salt is insoluble in ammonia.

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XCVI.—*Solubility Influences. Part IV. The Salting-out of Aniline from Aqueous Solutions.*

By SAMUEL GLASSTONE, JOAN BRIDGMAN, and WILLIAM R. P. HODGSON.

IN continuation of previous work (Part I, J., 1925, **127**, 2660; Part II, J., 1926, 2935; Part III, *ibid.*, p. 2939) on the "salting-out effect," the influence of various salts on the solubility of aniline in water has now been systematically investigated. It has already been shown that substances which can dissolve in the solute the solubility of which is being determined give abnormal results, and consequently the first stage in the present work involved the examination of the solubilities of various salts and sugars in aniline. The following salts were found to be almost insoluble in aniline at 25° : sodium, potassium, and barium chlorides; sodium, potassium, barium, and strontium nitrates; potassium chlorate, chromate, ferrocyanide, fluoride, acetate, oxalate, carbonate, and hydroxide; sodium, potassium, and magnesium sulphates; ammonium oxalate; and sodium citrate. These substances were all used either alone or in pairs in the quantitative investigation of the "salting-out" of aniline from its aqueous solution. Salts which are hydrolysed to give appreciably acidic solutions could not be used. The following substances were found to be more or less soluble in aniline :

lævulose, glucose, sucrose, lactose; lithium, ammonium, cæsium, and rubidium halides (the fluorides were not examined); sodium and potassium bromides and iodides; ammonium and lead nitrates; copper, zinc, nickel, cobalt, chromium, and cerous sulphates. The last six substances all appear to form addition compounds with aniline; some of these compounds have already been isolated (Tombeck, *Compt. rend.*, 1898, **126**, 967) and the others are now being studied.

Experimental.

The aniline used was obtained by the fractionation of a pure commercial specimen until a portion of constant boiling point was obtained. The salts used were the best commercial products and were, in general, not further purified. The salt solutions were made up by weighing the salt and water; a small quantity of aniline was then added and the mixture was well shaken at a temperature a few degrees above that at which the solubility was being determined. The liquid was then placed in a thermostat at 25° or 50° and allowed to stand until it had become clear. (This procedure was found to be more satisfactory than shaking the mixture at the temperature of the thermostat.) The sample of saturated solution for analysis was removed in a warmed pipette, transferred to a stoppered bottle, and weighed. The amount of aniline present was either estimated directly by the bromine method (Sutton, "Volumetric Analysis," 1924, p. 367), or else the solution was first diluted with water and the aniline distilled in steam; the latter procedure was only adopted when the salts present were likely to interfere with the former method of estimating aniline. Preliminary experiments on the analytical method, in which known weights of pure aniline were used, gave very satisfactory results.

The method of calculating the results was the same as used in previous work (*loc. cit.*); m and w represent the number of g.-mols. of added salt and of water, respectively, required to make a solution which will be just saturated with 1 g.-mol. of aniline at the temperature of the experiment. The so-called "hydration number," n, which is a measure of the salting-out effect of a g.-mol. of the salt, is equal to $(w - w_0)/m$ where w_0, the value in pure water, is 135·7 at 25° and 117·2 at 50°. The hydration numbers have been extrapolated, as before, to infinite dilution of the salt, and the values so obtained, which are often only approximate, are given in parentheses at the bottom of each "n" column. A few results only are given for those alkali halides which were found to be soluble in aniline, in order to show the general tendency in these cases.

Lithium chloride.			Lithium bromide.			Lithium iodide.		
m.	*w.*	*n.*	*m.*	*w.*	*n.*	*m.*	*w.*	*n.*
				25°.				
1·27	145·2	7·5	0·54	*128·2*	—	0·34	*125·7*	—
32·29	342·4	6·0	6·90	*133·1*	—	1·69	*113·3*	—
232·7	843·4	3·0	36·61	*118·8*	—	4·80	*70·9*	—
				50°.				
1·10	125·4	7·5	0·48	*114·0*	—	0·30	*110·2*	—
31·59	297·6	5·7	6·35	122·7	0·9	1·52	*101·5*	—
200·1	725·2	3·0	34·37	*111·4*	—	4·61	*68·0*	—
Sodium chloride.			**Sodium bromide.**			**Sodium iodide.**		
				25°.				
0·95	154·2	20·5	0·49	139·6	7·9	0·32	136·4	2·2
3·03	186·7	16·8	1·29	146·3	8·2	0·87	137·3	1·8
8·38	246·8	13·2	3·17	163·2	8·7	1·80	*134·6*	—
19·20	345·7	10·9	18·33	244·0	5·9	10·14	*126·6*	—
73·33	708·2	7·8	59·09	413·5	4·7	31·49	174·2	1·2
		(24)			(?)			(?)
				50°.				
2·66	163·7	17·5	0·44	123·8	15·0	0·28	120·0	9·9
7·44	219·0	13·7	2·80	143·9	9·6	0·76	120·6	4·5
31·82	411·8	7·8	17·15	228·1	6·5	25·52	141·2	0·9
					(18)			(13?)
Potassium chloride.			**Potassium bromide.**			**Potassium iodide.**		
				25°.				
0·74	148·4	17·2	0·43	140·4	10·9	0·30	137·2	4·9
2·11	166·6	14·6	1·16	146·8	9·5	0·77	*134·5*	—
5·33	199·4	11·9	2·63	156·8	8·0	1·59	*132·1*	—
10·43	245·1	10·5	6·88	174·8	5·7	3·62	*132·3*	—
30·89	383·5	8·0	27·57	273·7	5·0	22·68	139·7	0·2
		(22)						
				50°.				
0·64	129·2	18·7	0·37	121·5	11·5	0·27	119·9	10·1
1·91	150·9	17·6	2·35	140·2	9·8	0·69	119·9	3·9
4·93	184·4	13·6	6·25	162·6	7·3	3·07	*112·4*	—
16·85	278·9	9·6	25·28	251·0	5·3	20·80	128·0	0·5
					(14?)			(13?)
Rubidium chloride.			**Rubidium bromide.**			**Rubidium iodide.**		
				25°.				
1·13	143·2	6·7	0·75	*132·6*	—	0·55	*124·2*	—
7·20	194·6	8·2	3·80	140·6	1·3	2·30	*107·6*	—
39·96	326·8	4·8	19·58	181·5	2·3	5·82	*83·7*	—
				50°.				
1·00	126·7	9·5	0·66	*116·1*	—	0·49	*109·5*	—
6·61	179·1	9·5	3·52	130·2	3·6	2·12	*99·2*	—
38·17	312·8	5·1	18·51	171·5	3·2	5·58	*80·2*	—
Cæsium chloride.			**Cæsium bromide.**			**Cæsium iodide.**		
				25°.				
0·74	*132·2*	—	0·56	*126·3*	—	0·50	*116·9*	—
3·59	*134·7*	—	2·37	*111·5*	—	1·71	*98·5*	—
12·68	141·4	0·5	5·86	*84·6*	—	2·60	*69·2*	—
				50°.				
0·66	117·5	0·5	0·49	*110·9*	—	0·44	*105·8*	—
3·41	130·1	3·8	2·21	*104·2*	—	1·52	*87·2*	—
12·75	142·1	2·0	5·92	*85·4*	—	2·54	*67·4*	—

Ammonium chloride.			Ammonium bromide.			Ammonium iodide.		
			25°.					
1·05	140·9	4·9	0·49	*127·1*	—	0·34	*131·7*	—
5·82	155·1	3·3	5·23	*116·0*	—	2·82	*90·9*	—
13·94	162·2	1·9	11·93	*97·1*	—	7·31	*39·2*	—
			50°.					
0·95	127·6	10·9	0·43	*111·8*	—	0·30	*115·7*	—
5·42	144·3	5·0	4·76	*103·5*	—	2·41	*77·6*	—
13·72	163·1	3·3	11·15	*90·7*	—	6·25	*33·5*	—

The following results were all obtained at 25°.

Barium chloride.			Potassium nitrate.			Potassium chlorate.		
m.	*w.*	*n.*	*m.*	*w.*	*n.*	*m.*	*w.*	*n.*
0·26	142·8	28·2	0·50	138·0	4·6	0·20	137·3	7·9
0·48	148·8	27·1	1·34	142·9	5·4	0·42	139·4	8·8
0·59	151·7	27·3	3·04	153·4	5·8	0·63	140·3	7·2
1·37	169·6	24·8	5·33	169·4	6·3	0·86	141·8	7·1
3·88	218·6	21·3	8·31	186·5	6·1	1·11	142·9	6·5
		(29)			(?)			(11·5 ?)
Potassium acetate.			**Potassium carbonate.**			**Potassium hydroxide.**		
0·55	146·1	19·0	0·42	157·5	52·2	1·06	159·8	22·8
1·54	160·1	15·8	1·45	211·1	52·0	3·69	218·1	22·4
3·90	191·3	14·2	4·90	338·7	41·4	13·10	367·2	17·7
11·84	257·7	10·3	35·26	1084	26·9	78·28	975·0	10·7
30·04	250·6	3·8	502·9	7199	14·2	1055	6098	5·6
83·14	452·7	3·8			(72 ?)	4083	12730	3·1
		(23)						(29 ?)
Potassium chromate.			**Sodium nitrate.**			**Barium nitrate.**		
0·29	150·5	51·7	0·62	143·1	12·5	0·09	*133·8*	—
0·88	176·4	46·3	1·67	150·0	8·5	0·19	136·5	4·2
2·33	225·7	38·7	3·98	167·2	8·1	0·29	138·1	8·1
8·37	380·7	29·3	11·94	225·9	7·6	0·40	139·3	9·0
30·35	764·5	20·7	73·35	519·7	5·2	0·51	140·0	8·5
		(60)			(15 ?)			(?)
Strontium nitrate.			**Sodium sulphate.**			**Sodium citrate.**		
0·24	136·2	2·1	0·42	162·4	63·9	0·22	156·9	94·8
0·62	138·4	4·3	1·45	216·3	55·6	0·71	192·2	80·0
1·35	142·7	5·2	4·81	345·8	43·7	2·09	270·2	64·4
3·30	155·0	5·9	13·31	599·4	34·8	9·70	555·6	43·3
11·83	208·4	6·1			(74)	18·99	821·4	36·1
		(?)						(115)
Potassium sulphate.			**Potassium ferrocyanide.**			**Potassium oxalate.**		
0·15	145·3	63·1	0·19	183·7	250·2	0·35	155·9	58·2
0·33	155·0	59·0	0·40	171·9	91·0	1·08	189·4	49·7
0·76	177·3	54·5	1·04	213·7	74·8	2·92	245·4	37·6
2·09	232·6	46·3	3·58	334·8	55·6	9·14	422·0	31·3
		(72)			(350)			(70)
Magnesium sulphate.			**Ammonium oxalate.**			**Potassium fluoride.**		
0·47	158·0	47·1	0·21	144·5	41·7	1·07	168·9	31·1
1·62	201·7	40·7	0·44	153·4	39·9	3·84	235·7	25·6
5·00	300·2	32·9	0·73	162·3	36·5	14·12	410·6	19·5
30·29	1282	37·8	4·04	171·3	34·3			(35)
		(53 ?)			(46)			

The values of w are given in italics in those cases in which the salt causes the solubility of aniline in water to *increase*, hence it is seen that substances which are soluble in aniline (see p. 636) do not salt it out from its aqueous solution. This behaviour, as was the case with ethyl acetate (see Parts I and II), is most marked with iodides and nitrates, and, in fact, at 25° aniline is miscible in all proportions with a 60% solution of lithium iodide in water (compare Part I, p. 2665). We may assume, as before (Part II, p. 2935), that the "hydration number" of the iodide ion is zero, and so we may calculate the following values for the "hydration numbers" *per equivalent* of various ions at infinite dilution:

"Hydration" of Ions at Infinite Dilution.

Kations.				Anions.							
$Na^{\cdot}$	14	$NH_4^{\cdot}$	3	$Fe(CN)_6^{''''}$	75	C_2O_4''	23	$C_2H_3O_2'$	11	NO_3'	0
$K^{\cdot}$	12	$Sr^{\cdot\cdot}$	3·0	Citrate$'''$	24	F'	23	Cl'	10	I'	0
$Ba^{\cdot\cdot}$	4·5	$Mg^{\cdot\cdot}$	2·5	SO_4''	24	CrO_4''	18	Br'	5		
				CO_3''	24	OH'	17	ClO_3'	0		

The "hydration numbers" for most of the kations are distinctly unusual even when determined from experiments on salts which are insoluble in aniline; the abnormality may be connected with the basic nature of the aniline, or it may be due to the hydrolysis of the salts, but further discussion is unprofitable in the absence of sufficient information. For anions, however, the values given above bear a striking resemblance to those obtained from the experiments on the salting-out of ethyl acetate from its aqueous solution. It is again seen that, as a rule, high valency and small size tend to increase the salting-out power of an ion. Rothmund ("Löslichkeit," 1907, p. 152) has observed that, in general, the effect of a salt in reducing the solubility of a neutral substance is independent of the nature of the solute, and the results given above, calculated by a different method, show that this generalisation holds good, in a modified form, for the salting-out of ethyl acetate and aniline.

The Salting-out Effect of Mixtures.—The influence on the solubility of aniline of the following mixtures has been examined at 25°: sodium and potassium chlorides, sodium and barium chlorides, sodium and potassium nitrates, sodium and barium nitrates, potassium and barium nitrates, potassium chloride and nitrate, and sodium chloride and potassium nitrate. The results are given in terms of M_1 and M_2, representing the number of g.-mols. of each of the substances in the mixture (in the order named at the head of each table of results) which, when dissolved in w g.-mols. of water, form a saturated solution with 1 g.-mol. of aniline. The

values of $w - w_0$ determined experimentally, given in the columns headed "obs.," are compared with those calculated by the *second* method described in Part III of this series (*loc. cit.*). The agreement

M_1.	M_2.	$w - w_0$. obs.	$w - w_0$. calc.
Sodium and potassium chlorides.			
1·41	1·10	37·6	40·9
1·59	2·51	55·8	59·3
3·35	1·33	65·3	67·5
3·77	2·96	84·7	86·8
4·94	7·74	136·6	138·2
10·99	4·31	167·7	169·2
14·49	11·36	241·1	243·5
Sodium and potassium nitrates.			
0·80	0·68	9·6	9·5
0·87	1·48	16·4	13·7
1·77	0·75	18·8	17·9
1·89	1·59	24·7	24·1
2·20	3·70	40·7	40·2
4·48	1·88	46·3	46·9
5·36	4·51	66·8	67·1
Potassium chloride and nitrate.			
0·98	0·74	18·8	18·6
1·04	1·54	23·8	23·5
2·20	0·81	33·0	34·7
2·33	1·72	38·7	39·2
2·71	4·00	55·3	55·2
6·12	2·26	79·9	79·8
7·25	5·35	104·2	103·5

M_1.	M_2.	$w - w_0$. obs.	$w - w_0$. calc.
Sodium and barium chlorides.			
1·36	0·38	32·2	33·8
1·49	0·84	43·8	46·1
3·25	0·46	59·3	61·7
3·60	1·01	74·3	75·4
4·45	2·50	109·5	108·0
10·53	1·48	154·5	154·5
13·28	3·73	208·8	203·0
Sodium and barium nitrates.			
0·80	0·26	8·4	8·6
0·86	0·61	13·1	11·3
1·75	0·28	16·9	16·4
Potassium and barium nitrates.			
0·66	0·27	5·8	5·4
0·70	0·57	9·6	7·8
1·42	0·28	11·6	9·9
Sodium chloride and potassium nitrate.			
1·32	0·78	27·1	27·5
1·41	1·66	33·4	32·5
3·15	0·91	53·1	53·6
3·36	1·94	60·3	59·9
3·90	4·51	79·6	76·6
9·89	2·86	137·3	136·8
11·7	6·76	167·7	164·9

between the observed and the calculated values of the salting-out powers ($w - w_0$) of various mixtures confirms the conclusion therein reached, that "the salting-out power of a mixture is, in general, equal to the sum of the salting-out powers of the constituents, provided allowance be made for the electrical interaction of the ions."

Owing to the fact that so many common salts are soluble in aniline, it was not found possible to investigate the salting-out power of a complex ion, in order to compare the value with that of its constituents.

Summary.

(1) The solubility of aniline has been determined in aqueous solutions of a number of single salts, and of mixtures of salts.

(2) The results obtained confirm the conclusions reached as the result of previous work on the salting-out of ethyl acetate.

(3) The salting-out effect of anions on the solubility of aniline is almost identical with that on the solubility of ethyl acetate, but the results obtained with some kations are quite different.

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XCVII.—*Studies of Electrolytic Polarisation. Part VI. Electro-deposition Potentials of Alloys of Zinc with Iron, Cobalt, and Nickel.*

By Samuel Glasstone.

It has been known for some time (Toepffer, *Diss.*, Breslau, 1899; *Z. Elektrochem.*, 1899, **6**, 342; Küster, *ibid.*, 1900, **7**, 257; Treadwell, *Diss.*, Zurich, 1909, see Foerster, *Z. Elektrochem.*, 1911, **17**, 883; von Escher, *Diss.*, Dresden, 1912, see Foerster, *Z. Elektrochem.*, 1916, **22**, 85; Schoch and Hirsch, *J. Amer. Chem. Soc.*, 1907, **29**, 314) that if a gradually increasing current is passed through a solution containing a mixture of zinc and nickel or iron salts, the initial deposit on the cathode consists mainly of the iron-group metal but contains a small proportion of zinc. If the *C.D.* is increased a point is reached—at very low *C.D.*'s at room temperature, but at much higher *C.D.*'s at higher temperatures—at which the cathodic potential increases rapidly until it attains a value very close to that at which pure zinc would be deposited from a solution of the zinc salt only; the deposit under these conditions contains only a small proportion of nickel or iron. It was considered (Treadwell, *loc. cit.*) that the zinc deposited with the nickel increases the resistance to cathodic deposition which already exists in the case of the latter metal, with the result that a much higher negative potential is required to deposit the nickel; the result of the increased polarisation effect is that the deposit becomes richer in zinc until finally it contains only a small proportion of nickel. The results of von Escher suggested that the intensity of this polarisation depends on the hydrogen-ion concentration of the electrolyte, since the rapid rise of cathodic potential was found to occur more readily in a weakly acid than in a neutral solution of ferrous and zinc sulphates; hence hydrogen ions apparently enhance the retardation effect caused by zinc on the deposition of iron (see Grube, *Trans. Faraday Soc.*, 1914, **9**, 214; Foerster, "Elektrochemie Wässeriger Lösungen," 1922, p. 378).

In view of the results obtained previously on the electro-deposition potentials of iron, nickel, and cobalt, and their alloys (J., 1926, 2887, 2897) in solutions of varying hydrogen-ion concentration, it was of interest to investigate the changes of cathodic potential occurring with increasing *C.D.* in solutions of iron, cobalt, or nickel containing zinc ions, along the lines followed previously. The general observations of previous authors (*loc. cit.*) have been confirmed and found to apply to these solutions. Moreover, it has been found that, as in the case of anodic passivity, the *C.D.* may

be reduced considerably below that at which the sudden increase of potential occurs before the corresponding fall of potential results.

Experimental.

Electrolytic Solutions and Electrodes.—The solutions were generally made up by adding the requisite amount of zinc sulphate and either ferrous, cobalt, or nickel sulphate to a sodium acetate–acetic acid buffer mixture such as was used in previous work (*loc. cit.*); the total concentration of zinc and iron-group metal was 1 g.-equiv. per litre. The zinc sulphate was a recrystallised commercial specimen and the other salts were of the same quality as had been used before. The cathodes were of copper covered with a layer of iron, cobalt, or nickel, according to the metal in the electrolyte; the exposed area was generally 7·5 sq. cm. The anode was a short piece of platinum wire, and this was separated from the cathode by means of a porous pot when ferrous solutions were being used.

Potential Measurement.—Owing to the instability of the electrode potential in the vicinity of the *C.D.* at which the rapid increase of negative potential occurred, it was necessary to modify slightly the commutator–extrapolation method used in previous work. Preliminary experiments were made at a number of *C.D.*'s in order to determine the rate of fall of cathode potential in the first 0·012 sec. after the polarising current was switched off. The measurements were extrapolated in the usual way (J., 1924, **125**, 250) so that the potential at the instant of switching off the current could be determined and hence the fall of potential occurring in the first 0·002 sec.; this quantity was determined under a variety of conditions and never exceeded about 0·04 volt. In the actual measurements, the commutator was set so as to give the potential of the electrode at an average time of 0·002 sec. after the polarising current was stopped; the correction, found as described above, for the particular condition of the electrode was then added in order to give the values quoted below; these must be very close to the actual electrode potentials while the current was flowing.

As in previous work, the current passing through the electrolyte was increased or decreased by stages and kept constant for 1 minute before the potential was measured; the reference electrode was in every case a calomel half-element containing a saturated solution of potassium chloride and no allowance was made for liquid-junction potential.

Results.—The potentials recorded in Table I were obtained with a mixture of 0·1 g.-equiv. of zinc and 0·9 g.-equiv. of nickel in solutions of varying hydrogen-ion concentration at temperatures of 15° and 95°. (All *C.D.*'s throughout this paper are expressed in

terms of amps. $\times 10^{-4}$/cm.^{2}, and potentials are on the hydrogen scale.)

TABLE I.

Cathode potentials in 1Zn : 9Ni solutions.

	$N/50$-H_2SO_4.		p_H 2·8.		p_H 4·0.		p_H 5·5.	
C.D.	15°.	95°.	15°.	95°.	15°.	95°.	15°.	95°.
2·8	−0·19	−0·16	−0·32	−0·18	−0·41	−0·22	−0·47	−0·25
4·2	−0·22	−0·17	−0·41	−0·20	−0·45	−0·23	−0·50	−0·26
8·4	−0·28	—	−0·52	−0·24	−0·52	−0·25	−0·56	−0·30
12·0	−0·44	−0·21	−0·56	—	−0·56	−0·27	−0·79*	−0·32
20·0	−0·56	−0·23	−0·58	−0·28	−0·57	−0·31	−0·79	−0·34
32·0	−0·58	—	−0·60	—	−0·80*	−0·33	—	—
40·0	−0·80*	−0·26	−0·62	−0·31	—	—	−0·80	−0·42*
80·0	—	−0·29	−0·80*	−0·35	—	−0·35	−0·81	−0·43
160·0	−0·82	−0·30	−0·81	−0·37	−0·81	−0·39	—	−0·43
210·0	—	−0·43*	—	—	—	−0·43*	—	—
320·0	—	−0·43	−0·82	−0·38	—	−0·44	−0·83	—
640·0	—	−0·45	—	−0·42*	—	—	—	—
960·0	—	—	—	−0·43	—	−0·45	—	—

The general conclusions to be drawn from these results are that the potential of the electrode after the sudden increase has occurred —marked with an asterisk in Table I—is independent of the hydrogen-ion concentration of the solution, and that this potential rise occurs less readily, *i.e.*, at higher *C.D.*'s, at high temperatures and high hydrogen-ion concentrations.* Before the rapid increase of negative potential, the deposit on the cathode resembles ordinary electrolytic nickel in appearance and is not easily attacked by acids, but the metal deposited at the higher potentials is grey and dull, like electrolytic zinc, and is readily attacked by dilute acids, leaving a black residue of finely-divided nickel. This zinc-rich deposit obtained at 95° appears to contain relatively more nickel than does the corresponding deposit obtained at 15°, in agreement with the change in deposition potential from − 0·43 at 95° to − 0·80 at 15°. It should be noted that the first alloy, rich in nickel, is deposited at a potential of − 0·56 to − 0·58 at 15° and about − 0·30 at 95°; these are roughly the potentials at which pure nickel would be deposited from a solution of nickel sulphate alone at the concentration used in the mixture (J., 1926, 2887).

All these general observations have been confirmed by a large number of potential measurements made on various solutions of zinc sulphate and nickel, cobalt, or ferrous sulphate; it has also been found that the sudden increase of potential occurs at lower *C.D.*'s the greater the proportion of zinc to iron-group metal in the electrolyte. For solutions at the same hydrogen-ion concentration and temperature and containing the same relative pro-

* The anomalous result with $N/50$-sulphuric acid is probably due to the solution not being buffered.

portion of zinc, the zinc-rich alloy is deposited at lower *C.D.*'s in the case of nickel than in that of cobalt. With iron–zinc mixtures the zinc-rich alloy is only obtained at much higher *C.D.*'s; *e.g.*, in a solution of p_H 2·8 containing 1 atom of zinc to 9 atoms of iron (compare Table I), the sudden increase of potential occurs at a *C.D.* of about 210×10^{-4} at 15° and 640×10^{-4} at 90°. Once this higher potential condition has set in, however, the current may be reduced to very low values, especially at low temperatures, before the corresponding fall of potential is observed.

In order to compare the results obtained with different solutions, it was considered most satisfactory to determine a potential value equivalent to the deposition potential of the zinc-rich alloy for each solution; the nearest approach to this would be the cathodic potential of the electrode when the alloy was being deposited at the slowest possible rate. The following method was therefore adopted: The polarising current was increased to a fairly high value, so as to cause deposition of the zinc-rich alloy, and then reduced gradually; the potential was measured at each stage and found to decrease very slowly and then to remain almost constant before decreasing suddenly. This constant value was regarded as the deposition potential of the alloy of zinc and the iron-group metal. The observations were repeated at a number of temperatures and the results are summarised in Table II. The potential measurements

TABLE II.

Deposition potentials of zinc-rich alloys.

* Zn %. Iron–Zinc.	15°.	35°.	55°.	65°.	75°.	85°.	95°.
2·5	−0·80	−0·78	−0·73	−0·66	−0·58	−0·52	−0·50
5·0	−0·80	−0·79	−0·75	−0·69	−0·59	−0·53	−0·50
7·5	−0·80	−0·79	−0·76	−0·73	−0·69	−0·62	−0·53
10·0	−0·80	−0·79	−0·77	−0·75	−0·73	−0·70	−0·66
50·0	−0·78	−0·78	−0·77	−0·76	−0·75	−0·74	−0·73
Cobalt–Zinc.							
5·0	−0·80	−0·75	−0·68	−0·63	−0·57	−0·50	−0·41
10·0	−0·79	−0·75	−0·70	−0·66	−0·60	−0·52	−0·43
20·0	−0·79	−0·76	−0·72	−0·69	−0·65	−0·59	−0·49
40·0	−0·78	−0·78	−0·76	−0·75	−0·73	−0·70	−0·66
50·0	−0·78	−0·78	−0·77	−0·76	−0·75	−0·73	−0·70
70·0	−0·77	−0·77	−0·77	−0·76	−0·76	−0·75	−0·72
Nickel–Zinc.							
1·0	−0·80	−0·65	−0·55	−0·49	−0·45	−0·40	−0·38
5·0	−0·80	−0·69	−0·59	−0·54	−0·47	−0·41	−0·39
10·0	−0·79	−0·70	−0·62	−0·56	−0·50	−0·44	−0·42
30·0	−0·78	−0·74	−0·68	−0·64	−0·56	−0·49	−0·45
50·0	−0·77	−0·75	−0·72	−0·70	−0·67	−0·61	−0·56
70·0	−0·76	−0·75	−0·73	−0·71	−0·68	−0·63	−0·58
90·0	−0·76	−0·75	−0·74	−0·73	−0·72	−0·70	−0·65

* This gives the zinc in the electrolyte as an atomic percentage of the total zinc and iron-group metal.

were very consistent and, as indicated above, independent of the hydrogen-ion concentration of the electrolyte.

Discussion.

It appears very probable, from the results of the foregoing experiments, that the hydrogen-ion concentration of the electrolyte, contrary to the views of previous authors (see p. 641), plays no direct part in any influence which the simultaneously deposited zinc may have on the retardation of the electro-deposition of the iron-group metals. In general, the sudden increase of cathode potential, and the change in the nature of the deposit from an alloy rich in iron-group metal to one rich in zinc, occur at a lower *C.D.* the smaller the hydrogen-ion concentration of the solution; this is merely due to the fact that a given rate of metal deposition is more easily reached when the solution is less acidic, and not because the hydrogen ions accelerate the deposition of nickel, iron, or cobalt. It is doubtful, too, if the small amounts of zinc deposited with the iron-group metal at the low cathodic potentials appreciably affect the deposition of the latter; for the initial deposition of the alloy poor in zinc occurs almost at the same potential as that at which the iron, cobalt, or nickel itself would be deposited, and, further, if the zinc inhibited the deposition of nickel, we should expect the cathode potential to rise rapidly with increasing *C.D.* from the instant at which metal deposition first occurs, instead of remaining fairly low over an appreciable range of current (see Table I).

An alternative view is the following (nickel is taken as representing any of the three iron-group metals): A small quantity of zinc does not appreciably affect the deposition of the nickel, or, in terms of the views expressed in connexion with previous work (*loc. cit.*), it has no influence on the rate of transformation of metastable to stable nickel, although in the zinc-rich alloy this rate of change is probably affected. The initial deposit at low *C.D.*'s will probably contain relatively more nickel than is present in the solution, and as the *C.D.* is increased gradually the composition of the deposit, as judged from the potential measurements, will not vary appreciably; a point will be reached, however, at which the nickel ions cannot diffuse towards the electrode as fast as they are being deposited. In order to maintain the current, an increased proportion of zinc ions must be discharged and an alloy richer in zinc commences to be deposited; owing to the high overvoltage of hydrogen at a zinc electrode it is fairly certain that hydrogen evolution at this new deposit will be retarded, with the result that the efficiency of metal deposition is increased and still more zinc must be deposited. This process results in the rapid increase in

the proportion of zinc in the deposit and corresponds with a rapid rise in the cathodic potential almost up to that at which pure zinc is deposited; the deposit now consists of an alloy very rich in zinc and rarely contains more than about 20% of iron-group metal. Further increase in the *C.D.* should result in a much more gradual increase in the zinc content of the deposit, and at very high *C.D.*'s this may even decrease slightly owing to the depletion of the electrolyte in the vicinity of the cathode. It might be anticipated that at this point, or as a result of decreasing the *C.D.* whereby the solution near the cathode would once more contain a large proportion of nickel, the original process of the deposition of a nickel-rich alloy would recommence; this does not occur, however, and it is concluded, therefore, that in the zinc-rich alloy the change from metastable to stable nickel is considerably retarded, and so the latter metal cannot be deposited at its ordinary potential. On decreasing the *C.D.* far below the point at which the sudden increase of potential occurred, a corresponding fall is observed; this cannot be due to any change in the concentration of the electrolyte near the cathode because the current value is generally so low that diffusion cannot play any appreciable part, and the "diffusion layer" must be almost identical with the bulk of the electrolyte. The suggested explanation for the fall of potential is that on reducing the *C.D.* the deposit becomes richer in nickel, and consequently the hydrogen overvoltage steadily decreases until a point is reached at which discharge of hydrogen ions can occur so readily that the discharge of zinc ions is no longer necessary to maintain the flow of current. A smaller proportion of zinc in the deposit will cause the hydrogen overvoltage to fall still further and so the cathode potential falls fairly rapidly to a low value at which almost all the current results in the discharge of hydrogen ions, although a small amount of nickel may also be deposited.

At increased temperatures, the rate of diffusion of the electrolyte is increased and the hydrogen overvoltage is decreased, hence the rapid rise in potential occurs at a higher *C.D.* than at low temperatures. Since the normal rate of change of metastable to stable nickel is greater at high temperatures, it is to be expected that the zinc-rich alloy will contain relatively more nickel than at low temperatures; the deposition potentials, in accordance with this, are in most cases much lower than that at which pure zinc is deposited (see Table II; the deposition potential of pure zinc from a *N*-solution at 95° was found to be — 0·74 volt).

A close examination of Table II reveals a number of points of interest which cannot be discussed owing to lack of information on the nature and properties of the individual deposits, obtained at

different temperatures, from various solutions containing zinc and either iron, cobalt, or nickel.

Summary.

(1) It has been confirmed that during the electrolysis of a solution containing a mixture of zinc and nickel or iron the cathodic potential at some point rises rapidly and an alloy consisting mainly of zinc is deposited; the same phenomenon has also been observed with solutions of cobalt and zinc.

(2) The current density at which the sudden increase of potential occurs is generally smaller the lower the temperature, the greater the proportion of zinc in the solution, and the lower the hydrogen-ion concentration.

(3) The deposition potential of the zinc-rich alloy has been measured in solutions containing various proportions of zinc and iron, cobalt, or nickel at temperatures ranging from 15° to 95°; this potential decreases with increasing temperature.

(4) The theories of previous authors do not appear to explain adequately the results of the present work, and alternative suggestions have been made; the sudden increase of cathodic potential is attributed to a decrease in the concentration of the nickel, cobalt, or ferrous ions in the vicinity of the cathode, with the result that an alloy richer in zinc and with a high hydrogen overvoltage is deposited.

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XCVIII.—*The Molecular Conductivity of Cadmium Iodide in Acetonitrile.*

By FREDERICK KARL VICTOR KOCH.

CADMIUM iodide is of especial interest from the electrochemical point of view since both of its constituent elements show considerable residual valency in their compounds. The solutions of this salt therefore contain highly complex molecular and ionic species and have been the subject of considerable investigation (McBain, *Z. Elektrochem.*, 1905, **11**, 215).

The following results for the molecular conductivity of this compound in acetonitrile at 0° and 25°, and the calculated values of the temperature coefficients, not only furnish additional evidence of this complexity, but also allow certain general conclusions to be drawn as to the molecular state of cadmium iodide in these solutions.

Apparatus and Materials.—The bridge used was of the drum

type (Leeds and Northrup) and was 10 m. long, whilst the standard resistances were of the dial pattern (Cambridge and Paul). The alternating current was supplied by a valve oscillator, electromagnetically shielded from the rest of the apparatus. A variable condenser was placed in parallel with the standard resistance to balance the capacity of the conductivity cell. An excellent minimum was found (usually complete silence) and the readings could therefore be obtained with a high degree of accuracy.*

The conductivity cell was of the cylindrical type with vertical grey platinum electrodes and a ground-in stopper (Washburn, *J. Amer. Chem. Soc.*, 1916, **38**, 2431). The cell constant was determined by the method of Parker and Parker (*ibid.*, 1924, **46**, 312).

Acetonitrile (B.D.H.) was allowed to stand over solid potash for 2 or 3 days in order to remove acetic acid and moisture. It was then decanted on to calcium chloride and, after distillation, shaken with a very little phosphorus pentoxide for about a day. After a final distillation from the phosphorus pentoxide the product (b. p. 81·6°/760 mm.) had a specific conductivity of $0{\cdot}5—1{\cdot}0 \times 10^{-7}$ mho (Walden gives $\kappa = 0{\cdot}398 \times 10^{-6}$ mho).

Cadmium iodide (Analytical Reagent) was purified from iodine (which it contained in sufficient quantity to give yellow solutions in acetonitrile) by recrystallisation—once from conductivity water and twice from absolute alcohol. It was then dried over phosphorus pentoxide in a vacuum. Solutions of pure cadmium iodide in acetonitrile are colourless.

The most concentrated solution (approx. $N/10$) was made up by weight and the others, except the last three, by volume-dilution.

The following table, giving the specific conductivities of three of the intermediate solutions at 0°, which were made up by dilution from two different stock solutions of the same concentration, indicates the reproducibility of the results. (V indicates the volume of solvent containing 1 g.-mol. of cadmium iodide.)

	κ (mho).	
V (litres).	(1).	(2).
163·4	$1{\cdot}842 \times 10^{-4}$	$1{\cdot}858 \times 10^{-4}$
326·7	0·943 ,,	0·948 ,,
653·4	0·483 ,,	0·480 ,,

For the majority of the solutions, the error in Λ (which was calculated from the average specific conductivity) is estimated to be not greater than 0·5%. The values of Λ in the case of the three most dilute solutions are probably somewhat less certain owing to

* The author is indebted to Mr. A. R. Martin for the set-up and loan of the conductivity apparatus.

the increasing significance of the specific conductivity of the pure solvent.

The values for the density of acetonitrile used in calculating the dilutions were 0·8052/0° (Beilstein) and 0·7800/25° (this investigation).

The temperature coefficients are calculated by using the molecular conductivities at 0° and 25° of the same original solution, *i.e.*, a solution of the same weight-normal concentration.

At 0° ± 0·01°.			At 25° ± 0·01°.		
V (litres).	$\kappa \times 10^4$.	Λ.	V (litres).	$\kappa \times 10^4$.	Λ.
*10·21	24·05	24·57	*10·53	24·46	25·75
20·42	13·15	26·86	21·06	12·98	27·33
40·84	6·950	28·38	42·12	6·713	28·29
81·68	3·612	29·48	84·24	3·426	28·85
163·4	1·850	30·23	168·5	1·736	29·23
326·7	0·9454	30·87	337·0	0·8842	29·80
653·4	0·4815	31·46	673·9	0·4524	30·50
1321	0·2510	33·16	1363	0·2519	34·34
2696	0·1455	39·23	2788	0·1526	42·54
7816	0·05425	42·40	8069	0·06194	49·98

* Determination of the density of an approx. $N/10$-solution of cadmium iodide in acetonitrile has shown that if the dilution is expressed in terms of volume of solution instead of volume of solvent, the first values of Λ in the above table would both be increased by about 0·5%.

The temperature coefficients of the molecular conductivity calculated from the above data are: + 0·00192, + 0·000750, − 0·000127, − 0·000855, − 0·00132, − 0·00139, − 0·00122, + 0·00142, + 0·00338, and + 0·00715, for the ten dilutions, respectively.

The significant point is that the temperature coefficients of the molecular conductivity are positive in the most concentrated and in the most dilute solutions, but negative in the intermediate solutions. Similar anomalous behaviour has been observed by Franklin (*J. Physical Chem.*, 1911, **15**, 675) for solutions of potassium iodide in liquid sulphur dioxide.

Any complex molecular and ionic species in solution will tend to break up both with rising temperature and with increasing dilution. It seems, therefore, that in order to explain the anomalous changes in the temperature coefficient, it is necessary to assume the existence of *at least three* molecular (or complex ionic) species in solution, the intermediate one having the largest conductivity, owing either to its more extensive dissociation or to the greater mobility of its ions.

The molecular conductivity of the most dilute solution (V = 8069) at 25° is only 49·98, whilst the ionic conductivity of the iodine ion is 96 (Walden, " Elektrochemie nichtwässeriger Lö-

sungen," p. 186), so that the cadmium iodide cannot be regarded as completely dissociated even at a dilution of 8000 litres. It should be noted that the temperature coefficients of the molecular conductivity tend (for the last three solutions) with increasing dilution towards the value of the temperature coefficient of the fluidity of acetonitrile, *viz.*, 0·0113.

In conclusion, the author gladly takes this opportunity of expressing his thanks to Professor J. C. Philip, F.R.S., for his constant interest and advice.

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XCIX.—*On the Alleged Retardation of Certain Reactions by Light.*

By ARTHUR JOHN ALLMAND and ROBERT EDWIN WITTON MADDISON.

ABOUT twenty years ago, Trautz published some papers (*Physikal. Z.*, 1906, **7**, 899; *Z. wiss. Phot.*, 1906, **4**, 351; *Z. Elektrochem.*, 1907, **13**, 550) in which he discussed the possibility of the retardation of chemical reactions by light, supporting his deductions by a series of experimental observations. The dissertation published later by Thomas (Freiburg i. B., 1908) contains further details with regard to the latter. In all cases but one (the decomposition of hydrogen peroxide), the reactions studied were those between oxygen and an aqueous solution of some oxidisable substance. A manometric method was usually employed, solution and oxygen standing in contact with one another inside a vessel similar to a gas pipette, which was closed by a U-shaped manometer open on one side to the air. Several such pipettes were used simultaneously, each being enclosed in a glass sheath containing a certain filter solution, except that the pipette serving for the dark control experiment was contained in a galvanised-iron sheath filled with water. The whole set of pipettes with their sheaths was placed in a large vessel filled with water which stood near a window. The water was stirred from time to time and it was assumed that comparable temperature conditions were obtained, although, as the experiments in some cases extended over several days and nights, this appears doubtful. In any case, the results are said to have been reproducible. In some experiments (notably those with sodium sulphide solutions and red light), a shaking apparatus in a thermostat was employed.

The following remarkable results were claimed. Violet light

retards the reaction of oxygen with aqueous solutions of sodium sulphide, of sodium sulphite, and of pyrogallol, and with cuprous chloride dissolved in ammonia or in hydrochloric acid. Red light retards the decomposition of aqueous hydrogen peroxide, and the oxidation of cuprous chloride in hydrochloric acid, of aqueous pyrogallol, and of benzaldehyde. Below 23°, it also retards the oxidation of sodium sulphide, but above 25° it accelerates it. Green light retards the oxidation of solutions of cuprous chloride in ammonia, whilst both green and yellow light retard the oxidation of aqueous sodium sulphite. Almost equally striking results are reported with regard to the accelerating effects of light of different colours on the same reactions.

To explain these results, Trautz suggests that the observed velocity in the dark must be regarded as compounded of two opposed velocities, forward and back, and that these opposed reactions are affected in different degrees by light. If the reverse reaction is accelerated to a greater extent than the forward reaction, a net retardation will result on illumination. This view involves the consequence that the thermal (dark) equilibrium ultimately reached in the reaction concerned must be displaced by light. No evidence that this is so is brought forward, nor do the known facts of photochemistry suggest that such a displacement occurs frequently. Trautz leaves it open as to whether the reaction obeys the same laws of kinetics in the light as in the dark, with mere alteration of coefficients, or whether the total reaction in light is to be regarded as made up of separate light and dark reactions, superposed additively on one another.

Several reasons led us to carry out experiments on this subject. They were (1) the remarkable nature of the effects claimed, even when "colourless" solutions, with negligible absorption in the visible region, were employed; (2) the lack of confirmatory data on equilibrium displacement in light (not merely in these experiments, where the detection of the displacement might well be difficult, but in photochemical reactions generally); (3) the probability that, in some reactions at all events, *diffusion* rates were in reality being measured; (4) the facts that the detailed figures given by Thomas, are, in general, irregular when plotted, and that, in the experiments on the oxidation of sodium sulphide solutions, "retardation" by violet light was observed to have taken place *during the night hours* almost as frequently as during the day, whilst on several occasions "acceleration," not "retardation," was noted during the day hours (points which only become apparent when the data for an experiment lasting over several days are considered in detail); (5) the absence of any indication that the use of a particular

pipette did not in some way lead to specific results; (6) the fact that the degree of temperature control obtained did not seem adequate when the manometric method of following the rate of reaction is considered.

Experimental.

The majority of our experiments were carried out on the oxidation of sodium sulphite solutions, where the high transparency in the visible region, maintained during the whole reaction, ensures a uniform light field throughout the solution from start to finish. Instead of allowing the oxygen to diffuse into the solution, as did Thomas, we passed a brisk current of air through continuously, and any likelihood of a diffusion reaction being measured was thus eliminated. The type of reaction vessel used (a cell composed of quartz plates cemented on to the ends of a 7·5 cm.-diameter circular cavity drilled through a glass block) has been described elsewhere (J., 1925, **127**, 829). In the present case, the glass block was 5 cm. in thickness. Two holes bored through its upper surface into the central cavity served for the introduction of a thermometer and of the pipette for abstracting samples of liquid for analysis, whilst a similar hole passing through the side of the block into the interior of the cell at its lowest level had cemented into it a glass tube for leading in the air-stream. In front of this vessel was placed a combined water-cooling and filter cell of similar construction (four quartz plates alternating with three glass frames of thickness 1·0, 0·5 and 0·5 cm., respectively, the whole cemented together). Through the compartment of this cell nearest the light source (1 cm. in depth), a current of tap-water was kept continuously flowing, whilst the other compartments (0·5 cm. in depth) contained the filter solutions (or distilled water in other cases). The whole was placed in a wooden box, blackened inside, covered with tin foil outside, and furnished with sliding shutters on each of two opposite sides, for entry of the light beam and, when required, for inspection. Holes in the lid were provided for the air-supply tube, the thermometer, and the pipette, and also for an additional thermometer used to register the temperature in the box itself (outside the reaction cell). The air stream was produced by a motor-driven positive blower, and passed through a tube packed with activated charcoal, a simple calibrated differential flow-meter, and a wash-bottle filled with some of the sodium sulphite solution, before entering the reaction vessel. A steady rate of supply was maintained by regulating a resistance in the motor circuit, and by adjusting a screw-clip on a rubber connexion between the blower and the flow-meter. 150 C.c. of solution were generally employed.

The analysis was carried out by removing 5 or 10 c.c. in a pipette, running them into 20 c.c. of 0·1*N*-iodine, acidified with dilute hydrochloric acid, and titrating back with 0·1*N*-sodium thiosulphate.

For most of the experiments, the light source was a quartz mercury lamp, placed 13 cm. away from the front of the reaction cell. For red light, a 500-watt Osram lamp was employed at a distance of 18 inches, and an additional glass water-cooler was placed outside the box in the path of the beam. The temperature generally rose about 2° during a complete experiment. The thermometer in the box outside the cell was, of course, chiefly affected during the "light" period, but the temperature of the solution inside the cell rose more or less uniformly during both light and dark periods. In any case the results show that any temperature effect was negligible. The filter solutions used are given in the following table. They were far from being monochromatic but, in view of the nature of the experiments, no particular importance was attached to this.

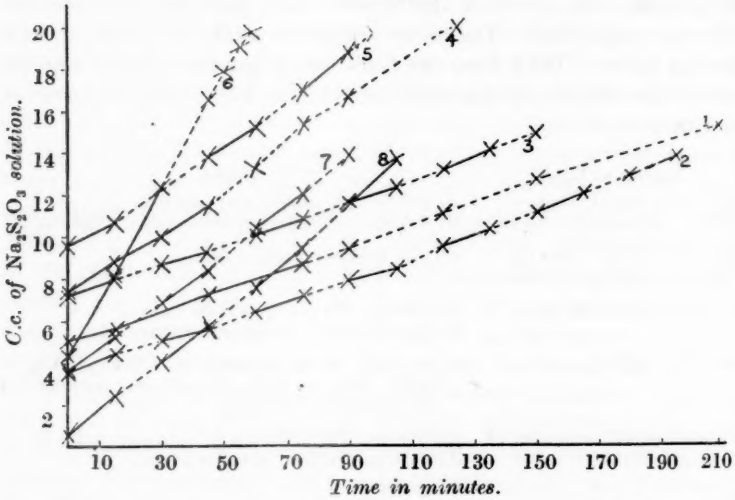
Nature of light.	Filter.
Short ultra-violet (below 265 $\mu\mu$—also visible light).	(*a*) 0·5 cm. *N*/1600-*p*-nitrophenol. (*b*) 0·5 cm. 0·002% *p*-nitrosodimethylaniline.
Long ultra-violet (365 $\mu\mu$—also some blue and violet).	0·5 cm. 0·0625% acid fuchsine.
Blue-violet (405—436 $\mu\mu$).	(*a*) 0·5 cm. 0·0125% acid fuchsine. (*b*) 0·5 cm. 0·2% quinine sulphate.
Green (500—550 $\mu\mu$).	1 cm. of an alcoholic solution of 2·4% $CoCl_2$ + 2·4% $NiCl_2$ + 0·1% fluorescein (similar to that used by Thomas).
Red (also small amounts of blue and violet).	(*a*) 0·5 cm. 10% ferrous ammonium sulphate. (*b*) 0·5 cm. 0·075% acid fuchsine.

Originally, alternate dark and light experiments, using different fillings in the cell each time, were carried out. The results were very discordant, successive runs on different portions of the same solution sometimes indicating an acceleration in light and sometimes a retardation. The difficulty of accurate control of the rate of dark oxidation of sodium sulphite solutions is well known and has recently been discussed by Rice from a new point of view (*J. Amer. Chem. Soc.*, 1926, **48**, 2099). We therefore altered our procedure and, without removing the solution from the cell, observed its rate of oxidation during successive dark and light periods, removing samples for analysis at the end of each of such periods. Under these conditions, the rate of dark oxidation remained reasonably constant when a particular cell filling was used. The variations in the slopes of the curves for different cell fillings show plainly the impossibility of obtaining conclusive results by the first method. Our data are

shown in the figure, where c.c. of 0·1*N*-sodium thiosulphate are plotted against time. Dark periods are shown by continuous, light periods by broken lines. Violet light was used in Expts. 1 and 2, red light in 7 and 8, green in 6, ultra-violet light of long wave-length in 3, and short wave-length ultra-violet light in 4 and 5. In plotting the results of 7 and 8, in order to separate the curves better, 4 c.c. have been subtracted throughout from the actual numbers used in the titrations.

In addition, a few experiments using red light were carried out with an apparatus similar to that of Thomas, the chief changes being that a straight mercury manometer was used, instead of the

FIG. 1.



U-tube type employed by him, and, in addition, that the pipettes were immersed in a thermostat at 25°. The solutions used were aqueous sodium sulphite and ammoniacal cuprous chloride—in both cases red light is said to accelerate the oxidation. Two pipettes were employed and the method of alternate light and dark periods was used. There is no need to give the results in detail. When manometer readings were plotted against time, regular curves were obtained with nothing whatever to indicate any accelerating effect of the red light.

Discussion and Conclusions.

It will be seen that, within the limits of experimental error, none of our results indicates any effect of light on the rate of oxidation of aqueous sodium sulphite with the exception of Expt. 4 and (more doubtfully) Expt. 5. In those cases, ultra-violet light of

short wave-length was being used, and the work of Mathews and his collaborators (*J. Physical Chem.*, 1913, **17**, 211; 1926, **30**, 414; *J. Amer. Chem. Soc.*, 1917, **39**, 635) has already shown that such light, which falls within the strong ultra-violet absorption band of sodium sulphite, accelerates its oxidation (compare the case of sodium bisulphite or metabisulphite—Baly and Bailey, J., 1922, **121**, 1813; Dietzel and Galanos, *Z. Elektrochem.*, 1925, **31**, 466; Getman, *J. Physical Chem.*, 1926, **30**, 266), This being the case, and taking into account the criticisms of the work of Trautz and Thomas made above, we are of opinion that the effects they observed were due, not to light, but rather to incomplete control of the dark reaction (such as would result from variable diffusion rates or variable amounts of positive catalysts associated with a particular filling or a particular pipette), and that, consequently, their results are probably spurious and cannot be regarded as evidence in favour of the possibility of photochemical retardation.

The above experiments were carried out during 1923. The junior author wishes to acknowledge his indebtedness to the Scientific and Industrial Research Department for a maintenance grant which enabled him to take part in the work.

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C.—*The Photodecomposition of Chlorine Water and of Aqueous Hypochlorous Acid Solutions. Part II.*

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IN Part I of this investigation (J., 1925, **127**, 822), we recorded our work on the factors affecting the proportions of the reaction products—oxygen and chloric acid. The present paper contains our results on the energetics of the reaction, and a suggested theory of the whole.

EXPERIMENTAL.

Extinction Coefficients.—These were determined by means of an ultra-violet spectrometer (Hilger), thermopile (Hilger), and galvanometer (Paschen), a quartz–mercury lamp being used as light source. The absorption cells were of the type already described (*loc. cit.*, p. 829), with crystal quartz ends. Two similar ones were employed, after being tested, when filled with distilled water, for equality of transmission over the wave-length range used.

One contained the solution under examination, the other distilled water; the ratio of the galvanometer deflexions therefore gave the fractional transmission of the solution. Cells of 5 and 0·5 cm. depth were used. No extraordinary accuracy is claimed for the results, in consequence of the difficulty experienced at that time in obtaining steady deflexions with the Paschen galvanometer at high sensitivity. Only those figures used in the subsequent calculations and discussion are therefore given. When values differed appreciably amongst themselves, those obtained from solutions with very low transmissions have been omitted. The units used are the mol., litre, and cm., together with Briggsian logarithms. The figures in the last two lines of the table we owe to Mr. H. J. Taylor.

TABLE I.

Solution.	Molecular extinction coefficient (k). 365 $\mu\mu$.	405 $\mu\mu$.	436 $\mu\mu$.
0·0145M-Cl_2	9·25	—	0·56
0·0375M-Cl_2	14·7	2·12	0·64
0·043M-Cl_2	—	2·43	0·74
0·0645M-Cl_2 + 0·01N-HCl	—	2·99	0·96
0·0115M-Cl_2 + 0·5N-HCl	—	7·51	2·7
0·045M-Cl_2 + 0·5N-HCl	—	3·85	1·38
0·051M-Cl_2 + 0·01N-KCl	—	2·9	1·16
0·045M-Cl_2 + 0·5N-KCl	—	5·1	2·1
0·0495M-Cl_2 + 0·01N-H_2SO_4	—	2·6	0·84
0·045M-Cl_2 + 0·5N-H_2SO_4	—	3·4	1·2
0·054M-Cl_2 + 0·01N-Na_2SO_4	—	2·3	0·74
0·047M-Cl_2 + 0·5N-Na_2SO_4	—	2·0	0·75?
0·049M-Cl_2 + Sat. Na_2SO_4	5·6	1·16	0·46
0·049—0·9M-HClO	1·2	0·19	0·13
0·045M-HClO + 0·5M-Na_2HPO_4	5	0·61	0·22?
0·024M-HClO + 0·125M-Na_2HPO_4	4·16	0·60	0·40
0·040M-HClO + 0·125M-Na_2HPO_4	3·59	0·43	0·37

In addition, k_{313} for 0·49—0·9M-HClO and for 0·0375M-Cl_2 were found to be respectively 18·2 and about 47.

Certain points in the table call for comment. In chlorine water, free from any addition, the values of k increase with concentration. The addition of hydrochloric acid increases k, and the more so the greater the ratio $[HCl]/[Cl_2]$. On the other hand, addition of sodium sulphate decreases the extinction. The last two effects are both visible to the eye. In all solutions containing chlorine, k_{405}/k_{436} is near 3. Solutions of hypochlorous acid have smaller k values than those containing chlorine, and k_{405} and k_{436} are nearer one another. The addition of disodium hydrogen phosphate increases the extinction. In all solutions examined, whether of chlorine or hypochlorous acid, the ratio k_{365}/k_{405} is of the order 5—9. We regard the effect on k of the addition of sodium phosphate to hypochlorous acid as independent evidence that, in such solutions, the reaction $HClO + HPO_4'' \longrightarrow H_2PO_4' + ClO'$

takes place to an appreciable extent (*loc. cit.*, p. 825). The increase in the extinction with increasing ratio $[Na_2HPO_4]/[HClO]$ would indicate k values for the hypochlorite ion greater than those for hypochlorous acid, and preliminary measurements indicate that k_{365} for this ion is about 9. The rise in extinction for chlorine solutions with increasing concentration is readily explicable by the changing degree of hydrolysis, the k values for chlorine being greater than those of hypochlorous acid. Assuming $K = [H^{\cdot}][Cl^{\prime}][HClO]/[Cl_2]$ to be $3{\cdot}8 \times 10^{-4}$ for our solutions (value interpolated from table on p. 508 of Lewis and Randall's "Thermodynamics"), we calculate the concentrations in the chlorine-water solutions given at the head of our table to be as follows:

(*a*) $0{\cdot}0035M$-Cl_2 + $0{\cdot}011M$-HClO (total $0{\cdot}0145M$).
(*b*) $0{\cdot}0185M$-Cl_2 + $0{\cdot}019M$-HClO (total $0{\cdot}0375M$).
(*c*) $0{\cdot}023M$-Cl_2 + $0{\cdot}02M$-HClO (total $0{\cdot}043M$).

Combining these data by means of the equation $\log I_0/I = d(C_{HClO} \cdot k_{HClO} + C_{Cl_2} \cdot k_{Cl_2})$, where d = the depth of the solution, with the measured transmissions of the solutions and the k_{HClO} values given above, we have calculated the values for k_{Cl_2} given in the second column of Table II. The remaining columns contain

TABLE II.

Wave-length.	In chlorine water.	k_{Cl_2}. For gas. (v. H. and S.).	(C. and R.).	(recent figs.).
313$\mu\mu$	(77)	53	33·6	—
365	34; 29	27	20·6	24·7
405	4·4; 4·1; 3·2	4	4·6	4·4
436	0·96; 1·29; 1·94	2	3·7	1·9

k values calculated for chlorine gas from (i) the accurate work of von Halban and Siedentopf (*Z. physikal. Chem.*, 1922, **103**, 71); (ii) some rough measurements made by one of us (P. W. C.) in conjunction with Dr. Reeve; (iii) more recent data obtained in this laboratory. The general nature of the agreement between the figures for dissolved and gaseous chlorine is of distinct interest.

Measurements of Quantum Efficiency.—A number of experiments were carried out, using one or another of several quartz–mercury lamps arranged to give "parallel" beams of known energy distribution and total energy flux, and filters intended to pass monochromatic radiation of wave-length 365 $\mu\mu$.

The energy absorbed in the reaction cell was computed by means of the extinction coefficients given above, and the quantum efficiency

calculated from the degree of decomposition. The exact experimental procedure used was varied during the course of the work, but in outline the method was as follows. The mercury lamp was situated immediately behind a metal screen in which was cut a circular aperture of 1—2 cm. diameter. This diaphragm was placed at the focus of a quartz lens (diameter, 8 cm.; focal length, 10—11 cm.), and the resultant approximately parallel beam passed through a water cell (for absorbing heat rays) and a cell containing the filter solution, before falling on the reaction vessel. The cells used were all of the type already described (*loc. cit.*, p. 829), their ends consisting of crystal quartz plates. The reaction vessel was 5 cm. deep in every case. Any chlorine carried forward by the evolved oxygen was, as before, trapped in a potassium iodide solution, and the necessary correction applied.

The intensities of the beams used were by no means uniform over their whole cross-section. In order to obtain the total incident energy flux on the surface of the reaction vessel, the filter cell was filled with distilled water, and the thermopile–galvanometer deflexion read with the thermopile placed in a number of representative positions in the path of the beam, and in the plane which was later occupied during the actual measurements by the front of the reaction vessel. The thermopile–galvanometer combination (in some experiments a Coblentz pile and Broca galvanometer, in others a Moll pile and Gambrell galvanometer) had previously been calibrated by means of a standard Hefner lamp. The average *H.K.* intensity of the unfiltered beam was thus obtained, and this, when combined with its measured energy-distribution, determined as described elsewhere (*J. Physical Chem.*, 1925, **29**, 713), with the spectral transmission of the filter used, with the insolated area of the solution under investigation, and corrected for reflexion at the front surface of the reaction cell, made it possible to calculate completely the intensity and the nature of the radiant energy flux entering the solution. The extinction coefficients of the different solutions were estimated for the beginning and end of the reaction by interpolation between the experimental figures already given, taking account of the change due to the production of hydrogen chloride by insolation. From these figures the initial and final absorptions were deduced, and the arithmetic mean was taken for the calculation of γ. In the case of chlorine in lithium chloride, no exact data were available, but both the appearance and photographs taken with a Judd Lewis photometer and quartz spectrograph indicated very high absorption.

Under the above experimental conditions, the lamps used gave beams of the following intensity and energy distribution.

TABLE III.

Lamp No.	Total intensity.	Fraction of total intensity. 313 μμ.	365 μμ.	405 μμ.	436 μμ.
1	25·9 *H.K.*	0·086	0·188	0·070	0·129
2	27·87	0·069	0·180	0·078	0·151
3	39·72	0·078	0·190	0·068	0·152

The filter employed for Expt. 1, Table V, consisted of 1 cm. of 0·03125% Diamond Fuchsine (Cassella). In Expts. 2 and 3, 5 mm. of 0·0625% Acid Fuchsine (B. D. H.) were used, and in Expts. 4—8, 5 mm. of a 0·075% solution of the same substance. This change from the Cassella to the B. D. H. dyestuff proved to be unfortunate, as subsequent measurements showed the latter to absorb diffusely, and to pass high proportions of the violet and blue lines. Although this unfavourable circumstance is partly corrected by the higher proportion of the 365 μμ component in the unfiltered beam, and by its greater absorption in the solutions used, the result is that the γ values obtained in these experiments are only average figures, corresponding to a mean wavelength which lies between 365—405 μμ and varies from experiment to experiment. The transmissions of the actual solutions (determined by the Hilger thermopile and Paschen galvanometer) are given in Table IV.

TABLE IV.

Expt.	Filter.	Fractional transmission of 313 μμ.	365 μμ.	405 μμ.	436 μμ.
1	1 cm. 0·03125% Diamond Fuchsine.	0·013	0·365	0·013	Nil.
2, 3	0·5 cm. 0·0625% Acid Fuchsine.	Nil.	0·234	0·333	0·115
4—8	0·5 cm. 0·075% Acid Fuchsine.	Nil.	0·175	0·267	0·075

The calculation is given in full for the simplest case only (Expt. 1) where the small amounts of absorbed energy belonging to lines other than 365 μμ were neglected (error involved about 2%).

Lamp used : No. 1. Fraction of 365 μμ energy absorbed : 1·0. Duration of expt. : 41·5 hours. Average surface of insolated solution : 31·6 cm.².
Energy in unfiltered beam incident on cell = a = 25·9 *H.K.*
Ergs in unfiltered beam incident on cell = a = 25·9 × 945/cm.²/sec.
Ergs of 365 μμ in unfiltered beam incident on cell = $b = a \times 0{\cdot}188$/cm.²/sec.
Ergs of 365 μμ in filtered beam incident on cell = $c = b \times 0{\cdot}365$/cm.²/sec.
Ergs of 365 μμ in filtered beam incident on solution = $d = c \times 0{\cdot}95$/cm.²/sec.
Ergs of 365 μμ in filtered beam incident on solution = $e = d \times 31{\cdot}6$/sec.
Ergs of 365 μμ incident on and absorbed by solution in course of run = $f = e \times 41{\cdot}5 \times 3600$.
Quanta of 365 μμ incident on and absorbed by solution in course of run = $g = f \div (6{\cdot}57 \times 822 \times 10^{-15})$.
$= 1{\cdot}40 \times 10^{21}$.
Molecules of chlorine decomposed in course of run = $0{\cdot}00366 \times 6{\cdot}06 \times 10^{23}$.
$= 2{\cdot}22 \times 10^{21}$.
Hence $\gamma = 2{\cdot}22/1{\cdot}40 = 1{\cdot}59$.

TABLE V.

No. of expt.	Lamp used.	Solution.	Initial conc. of $Cl_2(HClO)$. M.	Duration of insolation (hrs.).	Loss in titre by decomposition. M.	$HClO_3$ yield (%).	Initial fraction of incident energy absorbed. 365 μμ.	405 μμ.	436 μμ.	Final fraction of incident energy absorbed. 365 μμ.	405 μμ.	436 μμ.	Absorbed quanta (× 10^{-20}). 365 μμ.	405 μμ.	436 μμ.	Molecules decomposed (× 10^{-20}).	γ.
1	1	Cl_2 water.	0·0503	41·5	0·02305	46	1·0	—	—	As at start.			14·0	—	—	22·2	1·59
2	2	,,	0·02725	23·0	0·01515	62	0·977	0·466	0·172	0·984	0·499	0·198	7·01	2·37	0·65	20·35	2·03
3	2	,,	0·0550	30·0	0·02535	61	1·0	0·807	0·386	1·0	0·808	0·411	9·33	5·18	1·84	34·0	2·08
4	3	Cl_2 water +0·004N-HCl.	0·0405	27·0	0·0052	56	1·0	0·741	0·373	1·0	0·749	0·386	9·48	4·30	1·54	6·96	0·45
5	3	Cl_2 water +0·6N-HCl.	0·03775	48·25	0·0012	—	1·0	0·88	0·535	As at start.			16·93	9·07	3·87	1·61	0·054
6	3	Cl_2 water +0·5N-LiCl.	0·0440	46	0·00615	39	1·0	1·0	1·0	As at start.			16·15	9·83	6·90	8·24	0·25
7	3	Cl_2 water +0·33M-Na_2SO_4.	0·0330	26·75	0·0040	—	0·967	0·495	0·204	As at start.			9·08	4·30	1·54	5·36	0·42
8	3	HClO +0·125M-Na_2HPO_4.	0·05575	69	0·0300	86	0·872	0·226	0·204	0·695	0·156	0·112	19·0	2·8	1·6	40·2	1·72

Table V contains the results of our measurements, for which the accuracy claimed does not exceed 10—15%.

It will be noticed that γ for decomposition of chlorine water is much lowered by the addition either of hydrochloric acid or of the two neutral salts tested, results predicted by the observations of Bunsen and Roscoe (*Pogg. Ann.*, 1855, **96**, 373), Milbauer (*Z. physikal. Chem.*, 1914, **86**, 564), Benrath and Schaffganz (*ibid.*, 1922, **103**, 139), and others. The effect of the very small initial addition of hydrochloric acid in Expt. 4 is striking, and probably connected with the decreased yield of chloric acid remarked on in Part I of this work. Whilst, however, the addition of a chloride, besides lowering γ, decreases the yield of chloric acid and increases both extinction and the partial pressure of chlorine above the liquid, in the case of sodium sulphate the decreased quantum efficiency is accompanied by a decreased extinction and lowered partial pressure of chlorine, whilst the yield of chloric acid is practically unaffected (Part I, p. 834). Hypochlorous acid is seen to be, at all events, not more photosensitive than chlorine water under the conditions prevailing, whereas the reverse behaviour was originally anticipated (Part I, pp. 823, 824). It will be noted that γ in Expt. 1 is considerably lower than in Expts. 2 and 3. We think this may be connected with the low percentage of chloric acid found in the products, considerably the lowest of any ever obtained by us with chlorine water, and confirmed by several titrations during the course of the experiment. Qualitatively, it would suggest the presence of hydrochloric acid in the original chlorine water, perhaps due to insufficient washing of the gas.

Quantum Efficiency and Wave-Length.—Three experiments were carried out in which chlorine water was exposed under comparable conditions to monochromatic light of wave-lengths 313 $\mu\mu$, 365 $\mu\mu$, and 436 $\mu\mu$, of known relative, but not absolute, intensity. The filters employed were, respectively:

(*a*) 5 mm. of 0·0125% Diamond Fuchsine + 5 mm. of 0·0125% Auramine O.

(*b*) 1 cm. of 0·03125% Diamond Fuchsine.

(*c*) 5 mm. of 0·0857% Victoria Blue + 5 mm. of 4% quinine sulphate.

The results are in Table VI.

The figures stand in the usual order of increasing γ with increasing frequency, but we lay no stress on this, in view of the probable experimental error. The results might equally well be interpreted as indicating that γ is independent of λ.

TABLE VI.

Wave-length.	Relative incident intensity.	Average fraction absorbed.	Relative absorption rate (watts).	Initial titre. (M).	Loss in titre during 30 hrs.	Relative quanta absorbed.	Relative γ ($\gamma_{365}=1$).
313 $\mu\mu$	2·0	1·0	2·0	0·0445	0·0074	2·09	1·02
365	6·36	1·0	6·36	0·0515	0·0268	7·75	1·00
436	8·40	0·366	3·07	0·0497	0·0130	4·46	0·84

Discussion.

Any proposed reaction mechanism must account for the experimental facts described in this and in the preceding paper, of which the following are the most important.

(i) The yields of chloric acid during the photolysis of hypochlorous acid and of chlorine water are nearly the same; they are considerably increased by adding sodium phosphate, less so by lithium sulphate, slightly raised by sodium sulphate, and slightly diminished by sulphuric acid; they are depressed by adding strongly dissociated chlorides, which are effective in the order HCl>KCl>LiCl.

(ii) The same chlorides increase the extinction coefficients of chlorine water, the order of effectiveness now being LiCl>KCl>HCl. At the same time the partial pressure of the chlorine rises, as shown by the amounts volatilised during the insolations.

(iii) Lithium and sodium sulphates decrease both volatility of chlorine and extinction coefficient; the addition of sulphuric acid hardly affects the former, whilst slightly increasing k.

(iv) The three electrolytes so far tested (hydrogen chloride, lithium chloride, and sodium sulphate) all decrease γ_{365} for decomposition of chlorine water, the first being by far the most effective in this respect. γ_{365} for the photolysis of a hypochlorous acid solution containing sodium phosphate is lower than that for chlorine water.

(v) The actual value of γ_{365} for pure chlorine water under the conditions of experiment is about 2, and it varies but little with frequency between the limits 313—436 $\mu\mu$.

(vi) There is obviously a close similarity between the two photolyses.

Many possible reaction mechanisms have been considered and dismissed as involving unlikely assumptions or as leading to conclusions inconsistent with the experimental results. Thus, for hypochlorous acid photolysis, combinations of the following were considered.

	Mechanism.	γ.	Yield of chloric acid (%).
(a)	$\left\{\begin{array}{l}HClO + h\nu \longrightarrow HCl + O,\\ HClO + O \longrightarrow HClO_2,\\ HClO_2 + HClO \longrightarrow HClO_3 + HCl.\end{array}\right.$	3	100
(b)	$\left\{\begin{array}{l}2HClO + 2h\nu \longrightarrow 2HCl + 2O,\\ 2O \longrightarrow O_2',\\ O_2' + HClO \longrightarrow HClO_3.\end{array}\right.$	1·5	100
(c)	$\left\{\begin{array}{l}2HClO + 2h\nu \longrightarrow HCl + 2O,\\ O + HClO \longrightarrow HClO_2,\\ O + HClO_2 \longrightarrow HClO_3.\end{array}\right.$	1·5	100
(d)	$\left\{\begin{array}{l}2HClO + 2h\nu \longrightarrow 2HCl + 2O,\\ 2HClO + 2O \longrightarrow 2HClO_2,\\ 2HClO_2 \longrightarrow HClO_3 + HClO.\end{array}\right.$	1·5	100
(e)	$\left\{\begin{array}{l}HClO + h\nu \longrightarrow HCl + O,\\ O + HClO \longrightarrow HCl + O_2.\end{array}\right.$	2	0
(f)	$\left\{\begin{array}{l}2HClO + 2h\nu \longrightarrow 2HCl + 2O,\\ 2O \longrightarrow O_2.\end{array}\right.$	1	0

Similar schemes were considered for chlorine water, in which $Cl_2 + H_2O$ took the place of HClO, as also mechanisms involving as primary reactions dissociation of the chlorine molecule, either directly or after collision between an activated and a normal molecule.

We have finally been led to suggest the following reaction mechanisms.

	For hypochlorous acid.	For chlorine water.
A	$HClO + h\nu \longrightarrow HCl + O$,	$Cl_2,H_2O + h\nu \longrightarrow 2HCl + O$,
B	$\frac{1}{2}(2O \longrightarrow O_2')$,	$\frac{1}{2}(2O \longrightarrow O_2')$,
or C	$HClO + O \longrightarrow HCl + O_2'$,	$Cl_2,H_2O + O \longrightarrow 2HCl + O_2'$,
D	$HClO + O_2' \longrightarrow HClO_3$,	$Cl_2,H_2O + O_2' \longrightarrow HClO_3 + HCl$,
or E	$O_2' \longrightarrow O_2$.	$O_2' \longrightarrow O_2$.

By Cl_2,H_2O is meant, not necessarily a molecule of a "chemical" chlorine hydrate, but rather a grouping of molecules of these two substances in sufficiently close association to render possible the reactions ascribed to it.

The maximum attainable value of γ (processes A, C, D) will be 3, with a 100% yield of chloric acid. Processes A, B, E [(f) above] will result in $\gamma = 1$ and $HClO_3 = 0\%$; processes A, B, D [(b) above] in $\gamma = 1{\cdot}5$ and $HClO_3 = 100\%$; and processes A, C, E [(e) above] in $\gamma = 2$ and $HClO_3 = 0\%$. Let a be the fraction of absorbed quanta resulting in the process A, b and c the fractions of the total oxygen atoms produced by A reacting in accordance with B and C, respectively ($b + c = 1$), and d and e the fractions of activated O_2' molecules reacting in D and E, respectively ($d + e = 1$). Then it is clear that the observed quantum efficiency will be higher the greater a, c/b, and d/e, whilst the chloric acid yield will depend solely on d/e. The proposed mechanism thus allows of a very low γ value accompanying a 100% yield of chloric acid,

but, on the other hand, excludes the possibility of γ exceeding 2 unless chloric acid is produced. It also brings out clearly the essential similarity between the hypochlorous acid and chlorine-water photolyses.

Further consideration of these reaction stages suggests the probability that b is negligible compared with c, except in very dilute solutions (see later). We therefore put $b = 0$, $c = 1$, for purposes of calculation, and thus arrive at the simple relations

$$\gamma = 2a + ad = a(2 + d)$$

$$HClO_3 \text{ yield } (\%) = 100 \times 3ad/(2a + ad) = 100 \times 3d/(2 + d)$$

which, given γ and the chloric acid yield, allow us to calculate both a and d—or d alone, if only the chloric acid yield is available. Table VII contains, for the experiments of Table V, the values of a and d, whilst Table VIII contains d values for different solutions, calculated from the chloric acid yields given in Part I.

TABLE VII.

Expt.	1.	2.	3.	4.	5.	6.	7.	8.
a	0·67	0·80	0·83	0·18	0·026	0·11	0·17	0·61
d	0·37	0·53	0·52	0·47	0·1	0·3	0·53	0·81

TABLE VIII.

Solution.	HClO.	HClO+M/8-Na_2HPO_4.	HClO+M/4-Na_2HPO_4.	Cl_2 water.	Cl_2 water+2N-Li_2SO_4.
d.	0·52	0·81	0·73	0·52	0·65
Solution.	Cl_2 water +N/4-Li_2SO_4.	Cl_2 water +Na_2SO_4.	Cl_2 water +N/10-H_2SO_4.	Cl_2 water +N/2-H_2SO_4.	Cl_2 water +N/10-KCl.
d.	0·54	0·53	0·5	0·47	0·51
Solution.	Cl_2 water +N/2-KCl.	Cl_2 water +N/2-LiCl.	Cl_2 water +N/250-HCl.	Cl_2 water +N/100-HCl.	Cl_2 water +N/10-HCl.	Cl_2 water +N/2-HCl.
d.	0·22	0·3	0·47	0·46	0·22	0·1

The d *Coefficients.*—These express the fraction of O_2' molecules which collide with HClO molecules or Cl_2,H_2O groupings and thereby produce a molecule of chloric acid; $1 - d$ represents the fraction of such molecules which either undergo such a collision without result, or else become deactivated before collision. Clearly, if this mechanism holds good, the chloric acid yield would be expected eventually to diminish with fall of concentration, unless some kind of a compensating influence were active; and the shorter the average life of the activated molecule, the higher the concentration at which this effect would be anticipated. No definite sign of this falling off has so far been found in our experiments (*loc. cit.*, p. 833), which may indicate that the life of the O_2' molecule under the conditions prevailing was, in general, long enough to ensure a normally effective collision before deactivation. In dilute solutions

of chlorine water, however, a compensating influence of the kind mentioned may be active, *viz.*, an increased proportion of hypochlorous acid molecules resulting from greater hydrolysis, for the high *d* values with solutions of hypochlorous acid containing sodium phosphate suggest that hypochlorous acid molecules are better acceptors for O_2' molecules than are the Cl_2,H_2O groupings under the experimental conditions. Indeed, the difference is probably greater than appears from the above figures, for, as has been seen, there is reason to suppose that a proportion of hypochlorite ions, increasing with concentration of sodium phosphate, is present in these solutions, and other measurements point to their being comparatively bad acceptors for O_2' molecules.

The effect of *sulphates* is interesting, and can be considered in conjunction with the concomitant changes in the degree of volatility of the chlorine and in the extinction. We suggest that addition of sulphuric acid slightly increases the free chlorine concentration (when added in small amounts, at all events, in accordance with the Jakowkin equilibrium). The observed results are consistent with this view and with our hypothesis on the relative efficiencies of the acceptors HClO and Cl_2,H_2O. In the case of lithium and sodium sulphates, we assume the reaction $H^{\cdot} + SO_4'' \longrightarrow HSO_4'$ to take place, a change probably responsible for the results of Thomas and Baldwin (*J. Amer. Chem. Soc.*, 1919, **41**, 1981) on the effect of the addition of sulphates on the hydrogen-ion concentration (activity) in 0·1*N*-hydrochloric acid. This would cause the displacement of the Jakowkin equilibrium in the direction of increasing chlorine hydrolysis and a greater hypochlorous acid concentration; this, in turn, would account for the changes in volatility of chlorine, extinction, and yield of chloric acid.

The influence of *chlorides* is more complex. From a consideration of the data, it would appear to be two-fold—a lowering of the *d* coefficients due to the chlorine ion, and an opposed effect, depending on the kation, running parallel with an increase in extinction and volatility (*i.e.*, chlorine activity), and increasing as we pass from hydrochloric acid through potassium chloride to lithium chloride (order of increasing "hydration"). More will not be suggested at this stage, as we think that our results with chlorine water in chloride solutions need further elucidation and confirmation from several points of view. In addition, the formation of chlorine ions during insolation is a complicating factor.

The a *Coefficients.*—Those for chlorine water without any addition (Expts. 1—3) are seen to exceed that for hypochlorous acid in sodium phosphate solution (Expt. 8). In view of the fact that hydrochloric acid, which lowers these coefficients very considerably,

is produced during the reaction, it does not seem unreasonable to imagine that, if the effect due to this acid could be eliminated, a might be unity. It has already been mentioned that the nature of the results in Expt. 1 suggests that some acid was present from the commencement. Whether the lower value in Expt. 8 means that hypochlorous acid is primarily less photosensitive than chlorine water is doubtful. The presence of hypochlorite ions and also of the strong electrolyte sodium phosphate in the solution probably both play a part in lowering a. For we interpret the results of Expts. 3—7 in the sense that *strong electrolytes in general lower the efficiency of our primary photo-reaction resulting from quantum absorption.* Hydrochloric acid seems to be particularly effective, and 0·5M-lithium chloride more so than 0·33M-sodium sulphate. In this connexion, the marked retarding effect of chlorides, and particularly of hydrochloric acid, in photochemical reactions other than chlorine-water decomposition, is noteworthy. Examples are to be found in papers by Lemoine (*Ann. Chim.*, 1895, **6**, 433), Hatt (*Z. physikal. Chem.*, 1918, **92**, 513), Baur and Rebmann (*Helv. Chim. Acta*, 1922, **5**, 221), and Benrath and Obladen (*Z. wiss. Phot.*, 1922, **22**, 47, 65).

Finally, it may be remarked that the mechanism outlined above, if substantiated, will enable a clear distinction to be made (for the first time, as far as we are aware) between the *quantum efficiency* and the *quantum sensitivity* (respectively a and γ in this paper) as distinguished by Winther (*Trans. Faraday Soc.*, 1926, **21**, 608). Until this is confirmed, we have preferred to term γ the *quantum efficiency*, as is usual.

Thermochemical Relations.—For a to be unity, every absorbed quantum must cause reaction, which will probably only be the case if $Nh\nu$ is appreciably greater than the energy absorption required by the primary reaction per mol. of hypochlorous acid or of Cl_2,H_2O (Q). If they approach one another closely, then a value of a less than unity may be anticipated, although it is now generally agreed that Q may exceed $Nh\nu$ and reaction still occur in the case of absorbing molecules of particularly high individual energy content. In the present case we have (Thomsen's " Thermochemische Untersuchungen," p. 185) :

$$Cl_2 + H_2O \longrightarrow 2HCl + \tfrac{1}{2}O_2 + 10270 \text{ cals.},$$
$$HClO \longrightarrow HCl + \tfrac{1}{2}O_2 + 9380 \text{ cals.}$$

Assuming that

$$O_2 \longrightarrow 2O - 140000 \text{ cals.},$$

we get

$$Cl_2 + H_2O \longrightarrow 2HCl + O - 59730 \text{ cals.},$$
$$HClO \longrightarrow HCl + O - 60620 \text{ cals.},$$

these figures corresponding to $\lambda = 475\ \mu\mu$ and $\lambda = 468\ \mu\mu$ respectively. The longest wave-length used in our work was $436\ \mu\mu$, corresponding to 65040 cals. Hence it would appear that, as far as the size of the absorbed quantum is concerned, a should be unity in all cases. It will be remembered that our values of γ only showed slight and doubtful variations with wave-length between the limits 313—436 $\mu\mu$, which is in accordance with the above.

The C reactions are both strongly exothermic, apart from any excess energy derived from the primarily absorbed quantum which the oxygen atoms may carry. We have

$$HClO + O \longrightarrow HCl + O_2 + 79380 \text{ cals.},$$
$$Cl_2 + H_2O + O \longrightarrow 2HCl + O_2 + 80270 \text{ cals.}$$

Finally the D reactions, with *unactivated* oxygen, would both be somewhat endothermic :

$$HClO + O_2 \longrightarrow HClO_3 - 6000 \text{ cals.},$$
$$Cl_2 + H_2O + O_2 \longrightarrow HCl + HClO_3 - 5110 \text{ cals.},$$

but with the oxygen molecules carrying at any rate a proportion of the reaction energy liberated in C, their exothermic nature would appear highly probable.

Order of Reaction.—As long as the course of the reaction is represented by processes A, C, and D, the order will be between 0 and 1, increasing as the solution becomes more dilute, or as we pass from light of strongly absorbed to light of weakly absorbed wave-lengths. If, however, the solution becomes so dilute that B becomes more important than C, then n will increase still further. For the extreme case (c negligible compared with b), we have

(A) $-d[HClO]/dt = +d[O]/dt = k_a I_0 \varepsilon [HClO]$
(ε is the molecular extinction coefficient of HClO),
(B) $-d[O]/dt = 2d[O_2']/dt = k_b[O]^2$,
(D) $-d[O_2']/dt = -d[HClO]/dt = k_d[O_2'][HClO]$,
(E) $-d[O_2']/dt = k_e[O_2']$.

Whence, for the complete reaction,

$$-\frac{d[HClO]}{dt} = k_a I_0 \varepsilon [HClO]\left\{1 + \frac{k_d[HClO]}{2(k_e + k_d[HClO])}\right\}$$

which corresponds to an order greater than unity and increasing as [HClO] decreases. Any change in k_a, ε, etc., during insolation would of course complicate matters, *e.g.*, an increase in ε would decrease, or a decrease in k_a would increase, the apparent order of the reaction.

Certain experiments carried out under uniform conditions of illumination from start to finish, with titrations made at intervals,

have allowed of a calculation of the *average apparent* order of the reaction by means of the equation

$$(1/C_1^{n-1} - 1/C_2^{n-1})/(1/C_2^{n-1} - 1/C_3^{n-1}) = (t_1 - t_2)/(t_2 - t_3),$$

where C_1, C_2, C_3 represent concentrations at the times t_1, t_2, t_3. The results are in Table IX.

TABLE IX.

Expt.	Solution.	Light.	$t_3 - t_1$ (hours).	C_1 (normality).	C_3	n.
1	HClO.	Unfiltered.	4	0·114	0·070	0·25
—	,,	,,	4	0·091	0·052	0·6
2	Chlorine.	,,	23·25	0·067	0·001	1·2
3	,,	,,	23·5	0·084	0·003	1·2
4	,,	,,	22·25	0·056	0·001	1·2
5	,,	436 $\mu\mu$	36·25	0·099	0·069	1·0
6	,,	365 $\mu\mu$	31	0·103	0·048	0·0

Whilst demonstrating the complexity of the photolysis, they are in general agreement with the above deductions. In (6), the absorption is complete throughout, and the rate of reaction very uniform, in spite of the 50% decrease in concentration and the gradually increasing acidity, which would be expected to lower the quantum efficiency. On the other hand, in (5), where, in spite of the partial decomposition, the absorption slightly increases during the experiment (increase in ε), and where n was found to be very close to unity, it would seem that either the concentration or, more probably, the acidity effect (decrease in k_a) must be playing a compensating part. In (1) where absorption is only complete for the ultra-violet components of the light, n increases during the course of the reaction, although the absorption of visible light is also increasing (increase in ε). Here the same acidity effect appears to enter. And in (2), (3), and (4), where the rate of decomposition falls off rapidly towards the end of the reaction, it would seem likely that both k_a (acidity) and concentration influences play a part.

Further work is in progress from several points of view on the questions raised in this paper, particularly on the marked influence of hydrochloric acid on the course of the reaction, a factor which we consider responsible for the non-reproducible nature of some of the experiments, and on the general effect of strong electrolytes on our coefficients a and d.

Summary.

(1) Data are presented on the extinction coefficients of aqueous solutions of chlorine and of hypochlorous acid, both in absence and in presence of certain electrolytes.

(2) The results are recorded of quantum efficiency measurements made during the photodecomposition of such solutions.

(3) A detailed mechanism is suggested for such photodecomposition, which attempts to correlate the nature and proportions of the decomposition products with the observed quantum efficiencies, with the variations in the extinction of the solutions, with their chlorine partial pressures, and with the order of the reaction.

(4) This mechanism permits of the efficiencies of the primary and secondary reactions being separately determined, and allows of the analysis (up to a point) of the nature of the retarding effect exerted by strong electrolytes on the photodecomposition.

The experimental work in this paper was carried out during the years 1921—1924. Of the authors, one (P. W. C.) wishes to acknowledge the help afforded by a bursary granted him by the British Cotton Industry Research Association, and another (R. E. W. M.) similarly wishes to acknowledge the grant made him by the Advisory Council of the Department of Scientific and Industrial Research. Some of the quartz apparatus employed was purchased out of a grant made to the laboratory by Messrs. Brunner Mond and Co., Ltd., to whom we express our indebtedness.

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CI.—*On Active Nitrogen. Part II. Reactions with Gases.*

By ERIC JOHN BAXTER WILLEY and ERIC KEIGHTLEY RIDEAL.

IN a previous communication (J., 1926, 1804) evidence was presented for the assumption that active nitrogen represents a metastable molecule with the low mean energy content of *ca.* 43,000 cals./g.-mol. Experiments are now described upon the addition of gases—elementary, compound, and mixed—to the afterglow, and the bearing of these observations upon the energy content of active nitrogen is discussed.

The considerations underlying the various possible types of interaction between atoms and electrons noted by Franck, Klein, and Rosseland (*Z. Physik*, 1922, **4**, 41) have been extended by Franck and his co-workers to the case of interaction between excited atoms and molecules. In applying these considerations to the case of active nitrogen, the following possibilities are open:

(1) If the least radiation potential of the added gas be less than the energy of active nitrogen, the former may be stimulated to the

production of an excited molecule with the subsequent emission of its characteristic spectrum. Moreover, if its critical increment for dissociation, reaction, or decomposition also be less, chemical action may occur.

(2) If the lowest radiation potential of the added gas be greater than the energy of active nitrogen, the luminescence of the latter should be quenched to an extent depending on the nature and amount of the added gas. The excitation of certain spectra of metals, the dissociation of hydrogen examined by Franck (*Z. Physik*, 1922, **11**, 16), and the quenching of fluorescence with various gases examined by Wood (*Physikal. Z.*, 1912, **13**, 353) for mercury atoms excited by the line $\lambda = 2537$ are well-known examples of these cases.

Certain other possibilities, however, are present.

(3) The active nitrogen may react with the added gas or vapour to form a nitride, the necessary energy of activation for formation being less than the energy content of active nitrogen. If the resulting nitride be stable and its formation exothermic, the energy set free (which includes the heat of formation and the original energy content of the active nitrogen) may be dissipated as radiation—the phenomenon of chemiluminescence.

(4) Finally, reaction may take place between active nitrogen and molecules excited as in (1) to form an endothermic nitride which may subsequently undergo decomposition with the emission of radiation.

By applying these data upon the critical energy increments to observations of the effect of other gases upon the afterglow and the chemical reactions effected, we should be able to determine approximately the energy content of active nitrogen. The experiments show that with gases of critical energy increments below 55,000 cals./g.-mol. chemical action is always traceable, but it is only strong where the critical energy increment is *ca.* 43,000 cals. and under. Reliance has been placed upon chemical reaction rather than spectroscopic observations, the employment of the latter being inadvisable in view of the presence of so many possible disturbing factors, as has already been pointed out by one of us (*Nature*, 1926, **118**, 735). The latter value agrees closely with that put forward in our first paper.

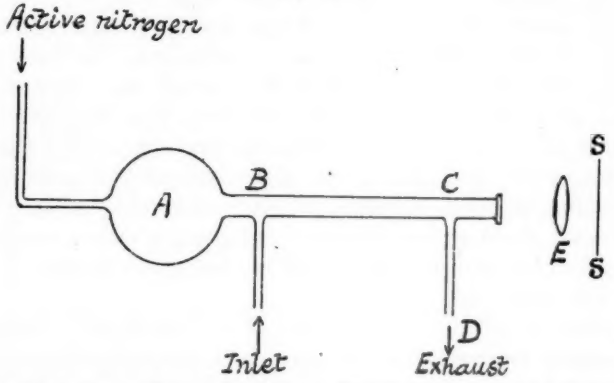
Experimental.

Active nitrogen was led from the discharge tube through the bulb, A (Fig. 1), to the tube, BC, which was some 25 cm. long. About 2 cm. along this tube a second tube was provided for the admission of the gases whose effects were to be studied, and the

mixture was drawn to exhaust at D. The end of BC remote from the active-nitrogen inlet was ground flat, and by means of a lens, E, the light in it could be focussed on the slit, SS, of a Hilger spectrometer. A series of condensing traps immersed in liquid air was placed in the exhaust line for the collection of any condensable products of the reactions taking place. The results are now given according to the considerations already advanced.

(a) *Hydrogen.* This gas is of interest in that its heat of dissociation is *ca.* 75,000—80,000 cals./g.-mol., and that it is readily activated or dissociated by collision with mercury atoms excited by the line $\lambda = 2537$. In agreement with Lord Rayleigh (*Proc. Roy. Soc.*, 1911, *A*, **85**, 219) we find that pure hydrogen has no

FIG. 1.



appreciable effect upon the glow. Examination of the gases condensed by cooling in liquid air after a run of 10 hours failed to show any trace of ammonia. Since, however, the evidence for the formation of ammonia on the admixture of nitrogen and activated hydrogen is conflicting,* the nitrogen–hydrogen mixture was

* The experiments of Wendt, Venkataramaiah, and Hirst all indicate that active hydrogen, produced either by the discharge or by Franck's method with excited mercury atoms, yields appreciable quantities of ammonia on interaction with nitrogen. On the other hand Bonhoeffer (*Z. physikal. Chem.*, 1924, **113**, 199) and Taylor (*Trans. Faraday Soc.*, 1925, **21**, 562) have failed to detect ammonia formation with active hydrogen. We have satisfied ourselves that if a stream of nitrogen at 10 mm. pressure be led into a stream of hydrogen at a point 150 mm. away from the end of the discharge tube through which hydrogen is flowing at the same pressure, appreciable quantities of ammonia are formed.

Mr. A. Caress, working in this laboratory, has recently obtained experimental evidence in support of the view that hydrogen atoms react with nitrogen to form ammonia at a catalytic metal surface but not in the homogeneous gas phase, a reaction which can be made to take place on excitation by electron collision.

passed over iodine, arsenic and sulphur (compare Wendt and Landauer, *J. Amer. Chem. Soc.*, 1922, **44**, 510), and also, after admission of oxygen, over phosphorus pentoxide in a weighed tube. In no case was any evidence obtained for the production of an active variety of hydrogen.

(b) *Oxygen.* This readily extinguished the luminescence with the production of heat. No evidence for the formation of nitric oxide or ozone was obtained. Also, with hydrogen–oxygen mixtures in various ratios, no indication of water formation over periods of 10 hours was obtained.

(c) *Carbon monoxide.* This gas merely dilutes the glow, behaving in this respect like nitrogen or hydrogen, as might be anticipated from the close similarity between carbon monoxide and nitrogen.

(d) *The halogens.* The characteristic blue luminosity of iodine is readily excited (compare Rayleigh, *loc. cit.*). The same holds true for bromine, the colour being brick-red. In the case of chlorine, the effect on the afterglow is much less marked; this, however, may be due in part to the fact that the spectrum of chlorine in the visible region overlaps the spectrum of the afterglow. The dissociation energies of the three halogens (in cals./g.-mol.) are: Iodine, 34,500; bromine, 46,200; and chlorine, 55,000.

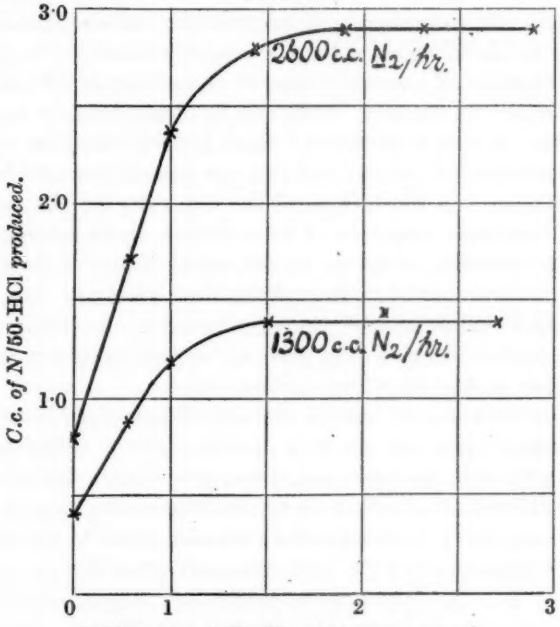
In no case could any condensate containing nitrogen and halogen be obtained by cooling with liquid air (compare Noyes, *J. Amer. Chem. Soc.*, 1921, **43**, 1774).

The effect of admitting a mixture of hydrogen and a halogen to the afterglow was examined for the production of hydrogen halides, but the results were negative with both bromine and iodine. With chlorine, however, the production of hydrogen chloride, together with minute traces of ammonium chloride and small quantities of a substance giving the characteristic reactions of chloroamine, was observed. Since this was the first instance of a chemical reaction being brought about by active nitrogen, similar to a hydrogen–oxygen reaction brought about by active mercury atoms, the case was examined in some detail.

When a mixture of hydrogen and chlorine was admitted to a stream of active nitrogen and the mixture drawn to exhaust through a U-tube cooled by liquid air, the gases which condensed gave a strongly acid solution in water, even when examined so rapidly as to preclude the formation of hydrogen chloride by reaction between the chlorine and the water. An absorption tube was then constructed in such a manner that the inlet tube terminated about 3 cm. above the bottom, and 10 c.c. of 15% neutral solution of potassium iodide were frozen into it. It was then immersed in liquid air and employed as a condenser as before. At the end of

the experiment, this tube was filled with nitrogen whilst still connected to the apparatus, sealed off, and warmed to allow the chlorine to be absorbed. It was then opened and the contents were washed out and titrated with neutral $N/50$-sodium thiosulphate until the iodine was removed, after which phenolphthalein was added and the whole titrated to neutrality with $N/50$-alkali, several c.c. being required. The presence of free hydrochloric acid was also proved (*a*) by titrating with $N/50$-sodium thiosulphate after addition of potassium iodide and iodate, and (*b*) by means of the hydrogen electrode.

FIG. 2.



Blank tests in which all conditions were the same as in the actual experiments, except that the nitrogen was not activated, gave no trace whatever of hydrogen chloride.

With constant nitrogen flow and constant composition of the hydrogen–chlorine mixture, the yield of hydrogen chloride was constant, and a few quantitative studies of its production were made. The results (Fig. 2) show that with a 1 : 1 mixture of hydrogen and chlorine the yield of hydrogen chloride increases with the quantity of the mixture added, but a limit is reached after which no further combination takes place.

The formation of hydrogen chloride may be ascribed to three

causes: (*a*) Reduction *in situ* by the hydrogen of an unstable nitrogen chloride. (*b*) Photochemical combination of chlorine and hydrogen under the influence of ultra-violet light emitted during the decay of the active nitrogen, probably with the formation of long chains to account for the relatively high yields of hydrogen chloride. (*c*) The production, by second-type collisions, of active chlorine molecules excited to a level sufficiently high to enable them to combine with hydrogen.

The first of these is contrary to the fact that Noyes (*loc. cit.*) was unable to prepare any nitrogen chloride by the action of active nitrogen upon chlorine even under the most varied conditions of flow speeds, etc. Decomposition of an unstable halide should be prevented by the addition of a large excess of chlorine.

In the absence of measurements of the absolute intensity of the active nitrogen luminosity, little can be done directly to prove or disprove the second hypothesis. Such a determination would give the total number of quanta emitted per second per unit volume of active nitrogen. A knowledge of the intensity of the part of the afterglow spectrum which is of wave-length short enough to bring about this synthesis, relative to the whole series of bands, would then give the number of quanta available for the reaction. Application of this value to the known data for the combination of hydrogen and chlorine would give an approximate estimate as to the probable yield of hydrogen chloride.

The third hypothesis is to a certain extent capable of analysis. It is possible, upon the assumption that every collision between molecules of active nitrogen and chlorine results in the formation of hydrogen chloride through the intermediate production of an active chlorine molecule, to calculate the probable yield of the acid. The number of collisions per c.c. per second is given by

$$n = 2\nu_1\nu_2(\sigma_1 + \sigma_2)^2\sqrt{2\pi kT(m_1 + m_2)/m_1m_2}$$

where ν_1 and ν_2 represent the number of molecules entering per second of active nitrogen and chlorine, respectively, σ_1 and σ_2 their diameters, and m_1 and m_2 their masses, and k and T have their usual significance. In a typical experiment a flow speed of 2600 c.c./hr. of nitrogen at *N.T.P.* was maintained, 1·5% of active nitrogen was present, and a 1 : 1 mixture of hydrogen and chlorine was admitted at the rate of $6{\cdot}2 \times 10^{-3}$ c.c./sec. 3·04 C.c. of *N*/50-hydrochloric acid were obtained in 30 minutes.

Hence $\nu_1 = 1{\cdot}5 \times 10^{-2} \times 2{\cdot}7 \times 10^{19} \times 2600/3600 = 2{\cdot}9 \times 10^{17}$;

$\nu_2 = 3{\cdot}1 \times 10^{-3} \times 2{\cdot}7 \times 10^{19} = 8{\cdot}3 \times 10^{16}$;

$\sigma_1 + \sigma_2 = 6 \times 10^{-8}$; $k = 1{\cdot}37 \times 10^{-16}$;

$m_1 = 1{\cdot}66 \times 28 \times 10^{-24}$; $m_2 = 1{\cdot}66 \times 71 \times 10^{-24}$.

Substituting in the equation, we obtain $15{\cdot}2 \times 10^{24}$ collisions/sec. between molecules of active nitrogen and chlorine.

Since the number of chlorine molecules entering per second is $8{\cdot}3 \times 10^{16}$, we see that every one will be hit several times every second; hence we may assume that all the chlorine molecules present are activated at least once.

The number of collisions between the hydrogen and chlorine molecules is similarly calculated to be $6{\cdot}2 \times 10^{24}$/sec.

Hence the number of collisions between the active nitrogen and chlorine molecules and between the chlorine and hydrogen is sufficient to warrant the assumption that yields of hydrogen chloride comparable with the concentration of active nitrogen should be obtained. This is the case, since the yield observed gives $2{\cdot}05 \times 10^{16}$ molecules/sec., whereas the active nitrogen flow is $2{\cdot}9 \times 10^{17}$ molecules/sec.

Hence we have considerable evidence that the production of hydrogen chloride is due to the formation of excited molecules of chlorine.

In searching for a reason why hydrogen chloride should be produced whilst neither hydrogen bromide nor iodide is formed, we may note that we are dealing with the stimulation only of the halogen to form an excited molecule, a condition comparable with the photochemical union between hydrogen and the halogens rather than with the thermochemical union. The photochemical union of the halogens is conditioned either by the heat evolution of the reaction $X + H_2 = HX + H$, as postulated by Nernst, or by that of the reaction $X_2' + H_2 \longrightarrow XH + H + X$, if the view be taken that the excited halogen molecule (X_2') is the reactive molecule. It is well known that the photochemical combination of hydrogen with chlorine, but not that of hydrogen with bromine or iodine, takes place at the ordinary temperature when the halogens are excited only to their threshold values for reaction, *i.e.*, in the visible portion of the spectrum. The fact that the halogens on excitation with active nitrogen yield banded rather than line spectra lends support to the hypothesis that the primary chemical reaction in the photochemical combination of a halogen with hydrogen is a reaction between an excited molecule of the halogen and hydrogen rather than the dissociation of the excited molecule into atoms with subsequent reaction. It does not, however, distinguish between the two possible reactions (1) $X_2' + H_2 \longrightarrow HX + HX'$, and (2) $X_2' + H_2 \longrightarrow HX + H + X$, although, from analogy with the thermal combination of hydrogen and bromine and from the existence of chains in the hydrogen–chlorine reaction, the reaction (2) appears more plausible than (1).

(e) *The hydrogen halides.* The halides HI, HBr, HCl form an interesting series in that the energies of activation for decomposition rise from the iodide to the chloride. From Bodenstein's data (*Z. Physik*, 1899, **29**, 295), the energy of activation for the thermal decomposition of hydrogen iodide can be computed as $E_{2HI} =$ 45,700 cals. For the other reactions, such data are not available, but it may be noted that hydrogen bromide decomposes in the homogeneous gas phase quite rapidly over the temperature range 400—750° K., which would indicate an energy of activation of about 40,000—50,000 cals./g.-mol. For hydrogen chloride, much higher temperatures are necessary (*ca.* 1400° K.) which would yield a value of $E_{2HCl} = ca.$ 90,000. If we compare the threshold radiation wave-lengths at which the percentage decompositions for the three halides are approximately identical, we obtain $\lambda = 4000$, 2800, and 2200 Å. for the iodide, bromide, and chloride, respectively. Since $E_{2HI} = 45{,}700$, those of the others must be of the order $45{,}700 \times 40/28$ and $45{,}700 \times 40/22$ or 65,000 and 83,000, respectively. We may assign values of the order of $E_{2HI} = 45{,}700$, $E_{2HBr} = 50{,}000$, $E_{2HCl} = 90{,}000$ without serious error. We should anticipate that both hydrogen iodide and hydrogen bromide might suffer decomposition, but not hydrogen chloride. This is found to be the case; the typical spectra of iodine and bromine were noted, whilst in the liquid-air trap both free halogen, ammonium halide, and traces of halogeno-amine were obtained. The reaction was *much* less marked with hydrogen bromide than with hydrogen iodide.

(f) *The oxides of nitrogen.* Both nitric oxide and nitrous oxide are of importance in this connexion. As has already been indicated (Part I, *loc. cit.*), the critical increment of nitric oxide is certainly below 55,000 cals., and in consequence the gas reacts with active nitrogen, undergoing decomposition to nitrogen and oxygen. In the case of nitrous oxide, we can, from the data of Hunter (*Z. physikal. Chem.*, 1905, **53**, 441) and of Hinshelwood (*Proc. Roy. Soc.*, 1924, **106**, 284) for the homogeneous bimolecular reaction, calculate an energy of activation of 60,300 cals./g.-mol. This gas was examined in the present experiments and did not affect the glow of active nitrogen. Moreover, when the gases, after admission of the nitrous oxide, were mixed with nitric oxide below the point where the afterglow ceases to be visible, no evidence of the formation of nitrogen peroxide in the liquid-air trap was found, indicating that no decomposition of the nitrous oxide had taken place

We have noted that hydrogen chloride, hydrogen, and nitrous oxide, with energies of decomposition of the order of 90,000, 85,000, and 60,000 cals./g.-mol., respectively, do not affect the

afterglow, and we may therefore conclude that the energy of active nitrogen is below these limits. Other gases of relatively large critical energy increments were likewise examined for their effect on the afterglow; these included water vapour, carbon dioxide, and carbon monoxide, with energies of activation of the order of $E_{2CO_2 \rightarrow 2CO + O_2} = 120{,}000$ cals./g.-mol. and $E_{2H_2O \rightarrow 2H_2 + O_2} = 110{,}000$ cals./g.-mol. In neither case was any effect other than a dilution observed.

Careful search for oxygen (by the admission of nitric oxide) and for cyanogen compounds in the former case, and for water and formaldehyde in a carbon monoxide–hydrogen mixture, revealed no evidence of chemical reaction.

We have seen that among the gases which are raised to a chemically reactive state we may include the halogens, and in the case of chlorine, of which the lowest critical increment for reaction with hydrogen is some 55,000 cals./g.-mol., only a part of the active nitrogen appears to be effective in promoting chemical action. This would set 55,000 cals. as the upper limit for the energy content of active nitrogen, whilst the experiment with nitrous oxide indicates that 60,000 cals. is well above the maximum.

Adopting a value of 150,000 cals. for the latent heat of evaporation of carbon (Thiel and Ritter, *Z. anorg. Chem.*, 1923, **132**, 151), we obtain for the linkage C–H (Fajans, *Ber.*, 1920, **53**, 643) a value of *ca.* 80,000 cals.; we should accordingly anticipate that methane would not be affected by active nitrogen. Lord Rayleigh (*Proc. Roy. Soc.*, 1915, **91**, 317) was of the opinion that methane underwent slight decomposition, a view to which König and Elöd (*Ber.*, 1914, **47**, 516) could not subscribe. Since small traces of other hydrocarbons readily react with active nitrogen, it is necessary to ensure their absence from the gas, and we have accordingly prepared pure methane from carbon monoxide and hydrogen by passage over a diatomaceous earth–nickel catalyst. This gas, which, after seven fractionations from liquid air, was free from carbon monoxide, did not affect the glow of active nitrogen, and no hydrogen cyanide could be detected in the gases after admixture of the methane. It may be observed that methane will undergo decomposition with a critical increment of only 55,000 cals. on a hot platinum wire (Schwab and Pietsch, *Z. physikal. Chem.*, 1926, **121**, 189) and a surface reaction between active nitrogen and methane is thus not impossible under the right conditions.

Ammonia is readily decomposed by active nitrogen into nitrogen and hydrogen; the critical increment here is probably quite low.

Conclusions.

In all the cases so far examined, chemical action as a result of second-type collisions, either between active nitrogen and the gas introduced or else as a "sensitised" reaction, occurs only when the critical increment of the second gas for the appropriate reaction is below 55,000—60,000 cals./g.-mol., and is strongest when this is about 45,000 cals./g.-mol. This is obviously a measure of the energy of active nitrogen, and is not incompatible with the view that in the afterglow we probably have a species of statistical equilibrium among three types of active molecules, some above, some below, and the majority upon the 2-volt level, an opinion which is supported by the spectroscopic evidence upon the afterglow. The three series of bands into which the true afterglow spectrum can be divided have intensities roughly in the ratio 1 : 2 : 1 for the red, yellow, and green, respectively, and the upper limit of the last-named bands coincides well with that observed for the limiting increment for reaction with active nitrogen (55,000—60,000 cals./g.-mol.). Moreover, if, as a first approximation, we regard these intensities as giving the relative concentrations of the three species, we see that with a gas of critical increment of, say, 55,000 cals./g.-mol., the extent of the reaction should be about one-fourth of that observed, all other conditions being left constant, with a gas for which the critical increment is 43,000 cals./g.-mol. and below. In the case of hydrogen and chlorine the yield of hydrogen chloride is about 1/14th of the active nitrogen concentration, and while the point cannot for obvious reasons be stressed, this observation is nevertheless significant.

These reactions are of course selective in nature and do not directly give a mean value for the energy of the active nitrogen, such as is obtained by the calorimetric method. Making due allowance for other necessary considerations as indicated, we see that the value originally given for the energy of active nitrogen is amply confirmed.

It is also interesting to note that Aakeson (*Lunds Univ. Arsskr.*, 1916, **12**, No. 11) found that 1·7-volt electrons undergo inelastic collision with nitrogen molecules, and whilst this value is most probably not correct to $\pm$ 1 volt, since no correction was applied for initial velocity, the existence of a level in the molecule at about that to be expected from an evaluation of the energy of active nitrogen would appear to be established.

It would here appear advisable, in view of the criticisms which have been directed against our contentions as to the energy content and nature of active nitrogen, to restate our case *in extenso* and

effect such agreement as is possible between our observations and the postulates of the spectroscopists (compare Johnson, *Nature*, 1927, **119**, 9).

In the preceding paper, on the assumption that one molecule of active nitrogen excites but one molecule of nitric oxide on reaction according to the schemes $N_2' + NO \longrightarrow NO'$ and $NO' + NO \longrightarrow N_2 + O_2$, it was shown that the calorimetric energy content of active nitrogen was equivalent to *ca.* 2·0 volts. In this paper, we have shown that chemical reaction is only effected by transfer of energy by second-type collisions from the active nitrogen to other gases when the requisite energy of activation lies below *ca.* 2·1 volts.

It is hoped to communicate similar conclusions from experiments on the catalytic decay of active nitrogen at the surface of metallic filaments, and from application of the Nernst heat theorem to the observations of one of us (Willey, *J. Soc. Chem. Ind.*, 1924, **43**, 260) on the iron nitride content of the vapours in an iron–nitrogen arc. It thus appears that for the purposes of chemical reaction active nitrogen only liberates energy equivalent to a 2·0-volt fall. We have regarded this as the total energy content of active nitrogen, for, as was pointed out in our first communication, there appears to be no reason why we should postulate the existence of several 2·0-volt falls in each molecule of active nitrogen. If, for example, the true energy content of active nitrogen is equivalent to 10 volts, then it will be necessary to postulate that one molecule can excite five nitric oxide molecules, transferring at each collision energy equivalent to *ca.* 2·0 volts. The same is true for the variety of chemical reactions recorded here : in no case do we find the active nitrogen transferring energy at one time equivalent to 4, 6, 8, or 10 volts, but always in 2-volt steps. Such steps in energy transfer apparently do not occur with excited mercury atoms, but if this suggestion for the reconciliation of spectroscopic and chemical data be true, it appears probable that the existence of successive 2-volt levels of some kind in the decay of active nitrogen should be capable of observation by spectroscopists.

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CII.—*The Effect of* gem-*Dialkyl Groups on the Formation and Stability of the Anhydrides of Dicarboxylic Acids.*

By Ernest Harold Farmer and Jacob Kracovski.

Reference has been made by various authors to the modifying effect of substituent alkyl groups on the ease of formation and the stability of the anhydrides of dicarboxylic acids. Auwers and Meyer (*Ber.*, 1890, **23**, 101), referring to the marked effect of alkyl substituents in the succinic and glutaric series and the failure of adipic acid to yield an anhydride, asked whether "durch Einführung mehrerer Methylgruppen in das Molekül der Adipinsäure eine Säure erhalten wird, welche der Anhydridbildung fähig ist," and Ingold (J., 1921, **119**, 308), dealing with the effect of *gem*-dialkyl groups on ring formation, pointed out that the same effect is equally apparent in heterocyclic ring-formation (lactones and glutaric anhydrides). It is clear from numerous incidental observations that in the succinic and glutaric series the ease of formation and the stability of anhydrides tend to increase with the number and size of substituted alkyl groups; even in the malonic series, in which the anhydrides, although capable of reacting as simple molecules, are almost certainly multimolecular, the correspondence of increased stability with increased substitution has been observed. How far this tendency extends is uncertain; many highly-substituted anhydrides of these series have not yet been obtained and at present comparisons are legitimate probably only between the members of a series. With members of different series, the hetero-structure of the ring presents difficulty; the extent to which the oxygen atom may relieve or transmit strain is unknown. Although in general an oxygen atom in a ring appears to function much as a carbon atom (leading to stability in the five- and six-membered anhydrides), yet there is a difference between homocyclic and heterocyclic rings in that the stability of the six-membered glutaric anhydrides increases with further substitution (compare Ingold, J., 1921, **119**, 952).

Any general attempt to compare anhydrides and homocyclic rings is confronted, when the adipic series is reached, by the problem of the close approach or the overlapping of the terminal groups. The possibility of obtaining stable, unimolecular anhydrides in this and higher series has not been explored. Consequently the nature of the factors tending chiefly towards stability, whether angular modifications as in the lower homocyclic rings, multiplanarity, re-entrant angles, or accommodative power of the oxygen atom, is

quite unknown. The anhydrides of various mono-, di-, and tri-alkyladipic acids have been obtained by Blanc and other workers. All of these pass into the corresponding ketones on heating, but no evidence as to their complexity is offered.

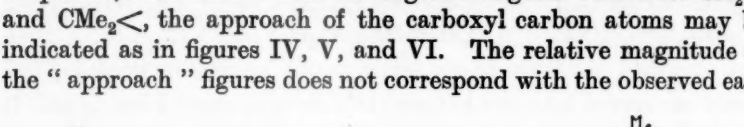
We have examined the anhydrides of adipic acid and of β-methyladipic acid. Both of these substances may be obtained in the pure condition and they are definitely unimolecular. They are distillable at low pressures without decomposition, but pass readily into the corresponding acids by absorption of moisture from the atmosphere. For the purpose of testing whether any considerable degree of stability may be conferred on the anhydrides of this series by the introduction of alkyl groups, two tetramethyladipic acids have been synthesised (J., 1926, 2318). Each of these acids (I and II) yields a crystalline, unimolecular anhydride. That of the ββ$\beta'\beta'$-acid is

$CMe_2 \cdot CH_2 \cdot CO_2H$	$CH_2 \cdot CMe_2 \cdot CO_2H$	$CMe_2 \cdot CH_2 > CO$
$CMe_2 \cdot CH_2 \cdot CO_2H$	$CH_2 \cdot CMe_2 \cdot CO_2H$	$CMe_2 \cdot CH_2$
(I.)	(II.)	(III.)

partly converted into the ketone (III) on prolonged heating and is readily hydrolysed by hot water. The highly crystalline anhydride of the αα$\alpha'\alpha'$-acid shows no tendency to pass into the corresponding ketone; it may be prepared by prolonged heating of the acid and is not hydrolysed by boiling water or aqueous sodium carbonate. Moreover, it yields an anilic acid with much greater difficulty than its isomeride. The two substances correspond roughly in properties with glutaric and di- or tri-methylglutaric acids respectively. Therefore it is evident, not only that substitution produces a considerable change in the stability of anhydrides in this series, but also that equivalent substitution causes effects varying with the position of substitution.

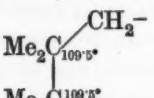
The abnormal effect of an α-substituent was observed by Ingold in studying ring-formation from bromo-α-methylglutaric acid (J., 1925, **127**, 387); here the introduction of an α-methyl group greatly hinders the formation of a *cyclo*propane ring. The abnormality was attributed to a " branched-chain " (volume) effect tending to open the valencies of the chain at the β-carbon atom. Short (*Chem. News*, 1926, **133**, 145), however, in criticising the suitability for comparing ring-forming tendencies of the method employed in this and other similar cases—that of hydrogen bromide removal from α-brominated esters—states that the inferior yield of the cyclic acid is probably to be attributed, in part, to the polar factors which control the ease with which the components of hydrogen bromide are removed. If the ready formation and superior stability of αα$\alpha'\alpha'$-tetramethyladipic anhydride are attributable to the " open-

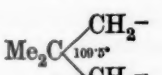
ing " effect caused by branching of the chain at the α-carbon atoms, it would appear that the properties of ααα′α′-tetramethyladipic acid in relation to adipic acid are in keeping with the " terminal approach" explanation of the inferior ring-forming capacity and anhydride stability of the latter. Further, the approach in stability of βββ′β′-tetramethyladipic anhydride towards that of ββ-dimethylglutaric acid would seem to have a rough correspondence with the almost identical distances (using Ingold's angular value for $CMe_2<$) between the terminal carbon atoms of the tetramethylbutane- (VIII) and dimethylpropane- (IX) chains. It would seem, however, that if a " branched-chain " effect is imagined to result from α-substitution, a similar effect might quite well be caused by the proximity of the *gem*-groups at the β-carbon atoms of βββ′β′-tetramethyladipic acid. If the carbon atoms of the adipic chain are regarded as uniplanar, then on the basis of Ingold's angular values for $CH_2<$ and $CMe_2<$, the approach of the carboxyl carbon atoms may be indicated as in figures IV, V, and VI. The relative magnitude of the " approach " figures does not correspond with the observed ease



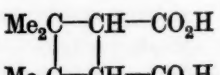
of formation and stability of the anhydrides and no better agreement is to be obtained by regarding a " branched-chain " effect (Fig. VII) as operative in the α-substituted acid. It is clear from such representations of members of the same and of different series of dicarboxylic acids that the powerful effect of *gem*-groups in promoting anhydride formation is not to be accounted for purely on the basis of tetrahedral angular modifications in a uniplanar carbon chain.

The above-mentioned approximation of the distances separating the terminal carbon atoms of the systems (VIII) and (IX) would suggest comparable tendencies towards *cyclo*butane ring-formation.

(VIII.) 



(IX.)



(X.)

By the action of alcoholic potash on α-bromo-βββ′β′-tetramethyladipic ester, 25% of the latter suffered replacement of bromine by

hydrogen. The remaining material appeared to undergo severe degradation, the products of which escaped identification; no trace of the *cyclo*butane acid (X) could be isolated. Attempts to prepare this cyclic acid from di*iso*propylidenesuccinic acid have likewise been unsuccessful. In view of the wide difference between the extents of cyclisation achieved with αα′-dicarboxyadipic ester (100%; Perkin, J., 1887, **51**, 18) and α-bromoadipic ester (1·5%; Ingold, J., 1921, **119**, 954) these results are possibly of little significance as an index to ring-forming capacity.

Other alkylated dicarboxylic acids are at present being examined.

EXPERIMENTAL.

Tetramethyladipic Acids.—These were obtained by electrolysis (Farmer and Kracovski, J., 1926, 2318). Since only about 12 g. of the ββββ′β′-acid could be accumulated, the experiments with this substance were of necessity carried out with small amounts of material.

Anhydride of ββββ′β′-*Tetramethyladipic Acid.*—Tetramethyladipic acid was heated for about 2 hours with three times the quantity of acetic anhydride theoretically required. The product was evaporated in a vacuum over caustic potash; a solid was then obtained which crystallised from petroleum (b. p. 60—80°) in long, colourless, flat needles, m. p. 189° (Found: C, 65·2; H, 8·55. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7%). The anhydride, which was very soluble in benzene, and moderately easily soluble in ether or petroleum, passed into the original acid (m. p. 207—208°) on warming with water. The molecular weight, determined cryoscopically in benzene, showed it to be of simple constitution (Found: *M*, 188. Calc.: *M*, 184).

The *anilic acid*, formed by treating a benzene solution of the anhydride with the calculated quantity of aniline dissolved in the same solvent, separated from hot chloroform as a crystalline powder (Found: C, 68·8; H, 8·1; *M*, monobasic, 281. $C_{16}H_{23}O_3N$ requires C, 69·3; H, 8·3%; *M*, 277).

1 : 1 : 2 : 2-*Tetramethyl*cyclo*pentan*-4-*one.*—The anhydride of the ββββ′β′-acid (2 g.) was refluxed for some time and then allowed to distil slowly. A small quantity of an oil (b. p. 186—189°) of strong camphoraceous odour was obtained. This substance readily yielded a semicarbazone, which crystallised from hot aqueous alcohol in shining plates, m. p. 223°. Comparison of the latter with a specimen (m. p. 223°) prepared by Francis and Willson's method (J., 1913, **103**, 2245) proved the identity of the two.

The anhydride of ααα′α′-*tetramethyladipic acid* was obtained in similar fashion to the ββββ′β′-anhydride. The crude, solid anhydride,

which was moderately easily soluble in benzene or ether but only very sparingly soluble in petroleum, crystallised from benzene–petroleum in long, colourless prisms, m. p. 166° (Found : C, 64·9; H, 8·5; *M*, cryoscopic in benzene, 180. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7%; *M*, 184). The *anilic acid* separated when a benzene solution of the calculated quantities of anhydride and aniline was heated and then kept. It was insoluble in water, but crystallised from hot chloroform in needle clusters, m. p. 218° (Found : C, 68·6; H, 8·4; *M*, monobasic, 282. $C_{16}H_{23}O_3N$ requires C, 69·3; H, 8·3%; *M*, 277). The anhydride was unaffected by boiling with water or even sodium carbonate solution. It dissolved, however, on boiling with strong caustic potash solution; acidification of the product precipitated the corresponding αα*α*′*α*′-acid (m. p. 191°). Slow distillation of the anhydride failed to yield the corresponding cyclic ketone, the substance distilling unchanged. Prolonged heating of the acid, however, prior to distillation caused partial conversion into the anhydride.

Anhydride of β-*Methyladipic Acid.*—β-Methyladipic acid, obtained by the oxidation of 1-methyl*cyclo*hexan-4-ol, was treated with acetic anhydride as above. The acetic acid and excess of acetic anhydride were removed at 15 mm. pressure; the syrupy liquid so obtained distilled at 165°/1 mm. without decomposition. The pure anhydride is a colourless syrup which readily hydrolyses in moist air (Found: C, 59·0; H, 7·15; *M*, cryoscopic in benzene, 140. Calc. : C, 59·15; H, 7·0%; *M*, 142).

The anhydride of adipic acid, obtained as above, was a solid, m. p. 97°. It distilled without decomposition at 1 mm. (Found: *M*, cryoscopic in benzene, 130. Calc. : *M*, 128).

Ethyl α-*Bromo*-ββ*β*′*β*′-*tetramethyladipate.*—The ββ*β*′*β*′-acid (3 g.) was converted into the acid chloride by warming with the requisite amount of phosphorus pentachloride. Bromine (1 mol.) was gradually added to the product. When the absorption, which took place readily, was complete, the mixture was poured into well-cooled alcohol. After 12 hours, the bromo-ester was precipitated by means of water and obtained as a yellow oil. It was not distilled, owing to the small quantity available, but was kept for several days in an evacuated desiccator before being analysed (Found : Br, 22·8. $C_{14}H_{25}O_4Br$ requires Br, 23·7%).

Action of Concentrated Caustic Alkali Solution on Ethyl Bromotetramethyladipate.—The bromo-ester (5 g.) was warmed and then poured into boiling 6*N*-methyl-alcoholic potassium hydroxide (20 c.c.). Potassium bromide separated at once. Heating was continued for a short time; the product was then cooled, diluted with absolute alcohol (40 c.c.), and filtered. The solid material was washed with

alcohol until only inorganic salts remained, the washings being added to the filtrate. Free caustic alkali was removed from the filtrate by saturating it with carbon dioxide and filtering. The alcoholic filtrate was evaporated to dryness and the residue was treated several times with water and evaporated to dryness. A solution of the final residue in a small amount of water was filtered through a wet filter-paper to remove a small amount of neutral oil and then acidified with dilute hydrochloric acid, ββββ′β′-tetramethyladipic acid being precipitated; a further small quantity separated when the acid solution was concentrated, the total yield (allowance being made for the slight deficit of bromine in the bromo-ester employed) being 25% of the material taken. The filtrate was finally evaporated to dryness in a vacuum, and the residue extracted with acetone. By this means a yellow syrup was obtained which, absence of severe degradation being assumed, represented about 50% of the material taken. After standing for nearly a year, the syrup deposited an acid which was readily soluble in water and separated from acetone–petroleum in colourless prisms, m. p. 212°. Owing to the very small quantity obtained, the acid could not be identified. Its low equivalent showed, however, that it was not the *cyclo*butane acid (X).

The residual syrup could not be solidified. It was distilled to free it from traces of inorganic matter, the distillate being collected in three portions. None of these reduced alkaline permanganate solution, and each had an equivalent weight and a carbon content much lower than those of the *cyclo*butane acid or hydroxytetramethyladipic acid. The syrup was almost certainly a mixture of acids, probably produced by severe degradation of tetramethyladipic acid.

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CIII.—*The Condensation of* p-*Hydroxybenzoic Acid with Chloral.*

By FREDERICK DANIEL CHATTAWAY and FERNANDO CALVET Y PRATS.

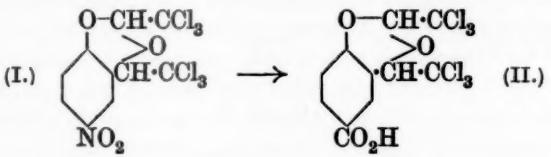
IT has recently been shown (J., 1926, 2720) that *p*-nitrophenol reacts with chloral in presence of concentrated sulphuric acid in a complicated and unexpected way, the final product being anhydro-

5-nitro-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (I), the constitution of which was shown by its yielding 5-nitro-2-ethoxyphenylglycollic acid on treatment with alcoholic potash.

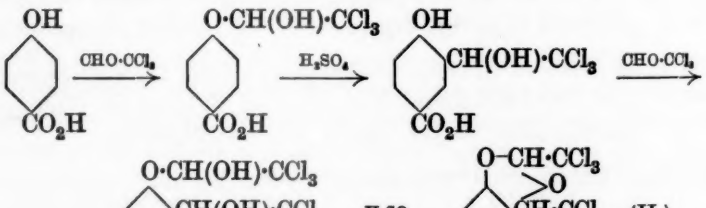
In similar circumstances, chloral reacts equally readily with *p*-hydroxybenzoic acid, giving a very stable and well-crystallised product, 2 mols. of the aldehyde condensing with 1 mol. of the acid, with loss of a molecule of water:

$$C_7H_6O_3 + 2CCl_3{\cdot}CHO - H_2O = C_{11}H_6O_4Cl_6.$$

The constitution (II) of the compound formed is similar to that of the condensation product (I) yielded by *p*-nitrophenol, since it can also be formed from the latter by replacement of the nitro-group by carboxyl through the amino- and the cyano-group.

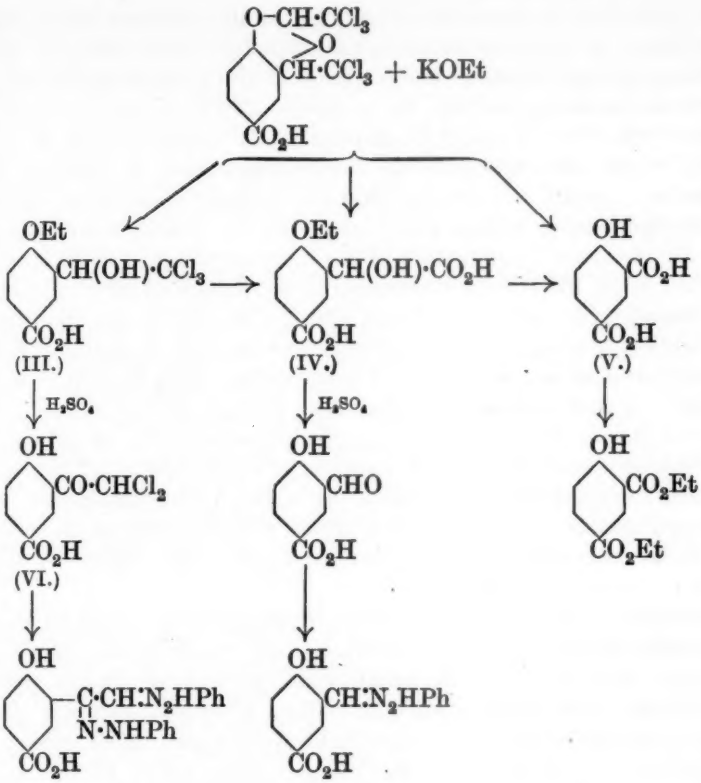


Since in the formation of the compound from chloral and *p*-hydroxybenzoic acid the carboxyl group remains unaffected, a condensation with the phenolic hydroxyl must first occur and be followed by intramolecular rearrangement. The hydroxyl group being thus re-formed, a second condensation of the same type must occur and be succeeded by elimination of water, thus,



the final product being *anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene*.

Its constitution is confirmed by its behaviour with alcoholic potash, with which it yields a mixture of *5-carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene* (III), *5-carboxy-2-ethoxyphenylglycollic acid* (IV), and *2-hydroxy-1*: *5-isophthalic acid* (V). These compounds were identified as shown in the following scheme:



EXPERIMENTAL.

Preparation of Anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (II).—(a) *By condensation of p-hydroxybenzoic acid and chloral.* A solution of 50 g. of *p*-hydroxybenzoic acid (1 mol.) and 150 g. of chloral hydrate (3 mols.) in 500 c.c. of concentrated sulphuric acid was kept at the ordinary temperature, with frequent shaking, for 3 days. The liquid had then become a pulp owing to the separation of the condensation product mixed with metachloral formed by the action of sulphuric acid upon the excess of chloral present (Byasson, *Compt. rend.*, 1880, **91**, 1071). The whole was poured into about 3 litres of water containing ice, and the solid which separated was filtered off and dried on the water-bath. The condensation product was extracted in a Soxhlet apparatus with ether, in which metachloral is insoluble. The ethereal solution was dried, the ether distilled off, and the condensation product obtained by crystallising the colourless, crystalline residue (yield, 46 g.) three times from ether–light petroleum.

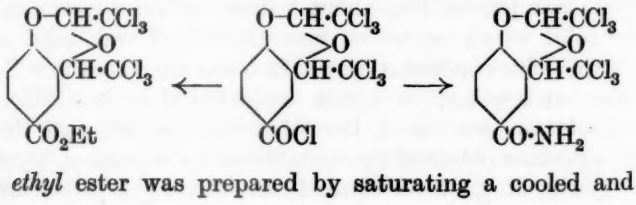
It is insoluble in water but moderately easily soluble in hot alkaline solutions. It dissolves easily in the ordinary organic solvents such as ether, alcohol, benzene, and acetic acid and separates from any of these in colourless needles, m. p. 225·5—226·5° (Found: C, 32·1; H, 1·6; Cl, 51·4. $C_{11}H_6O_4Cl_6$ requires C, 31·8; H, 1·4; Cl, 51·3%).

(b) *From the corresponding 5-nitro-compound* (I) *through the 5-amino- and 5-cyano-derivatives.* Anhydro-5-amino-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (10 g.), obtained by reduction of the corresponding nitro-compound (I) (J., 1926, 2725), was suspended in a mixture of 40 c.c. of concentrated hydrochloric acid and 180 c.c. of water and diazotised by adding, during 2 hours, the requisite amount of sodium nitrite dissolved in 30 c.c. of water, the temperature being kept at — 5° to — 10°. The diazotised solution was poured slowly into a concentrated solution of 40 g. of copper sulphate and 50 g. of potassium cyanide in about 100 c.c. of water kept at 45—50°. (If the temperature is allowed to rise above this limit, a considerable amount of tarry matter is formed.) The *nitrile*, which separated on cooling as a microcrystalline mass, was extracted with ether. A yield of 2·1 g. was obtained.

Anhydro-5-cyano-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene is an odourless solid which is not volatile in steam. It is insoluble in water, sparingly soluble in low-boiling petroleum, and easily soluble in boiling ether and alcohol. It is best recrystallised from ether–light petroleum, from which it separates in colourless needles, m. p. 159·5—160·5° (Found: Cl, 53·95. $C_{11}H_5O_2NCl_6$ requires Cl, 53·8%).

The nitrile was easily hydrolysed to the corresponding acid (II) by heating it for a short time with somewhat dilute sulphuric acid. A mixture of 1·3 g. of the nitrile, 30 c.c. of water, and 45 c.c. of concentrated sulphuric acid was heated to gentle boiling for about 20 minutes. On cooling and diluting the solution with water, the acid separated as a microcrystalline solid. It crystallised from warm ether–light petroleum in colourless needles (yield, 1 g.), m. p. 226°, identical with those obtained in method (a) (Found: Cl, 51·1%).

The Ethyl Ester, Acid Chloride, and Amide of Anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene.



—The *ethyl* ester was prepared by saturating a cooled and con-

centrated alcoholic solution of the acid with dry hydrogen chloride and heating it in a sealed tube for some hours. The ester separated in colourless crystals on cooling. It was recrystallised from hot alcohol, in which it was moderately easily soluble and from which it separated in small, colourless, rhombic plates, m. p. 100·5—101·5° (Found : Cl, 48·3. $C_{13}H_{10}O_4Cl_6$ requires Cl, 48·1%).

The ester was also obtained by boiling the acid chloride, described below, with alcohol.

The *acid chloride* was obtained by gently heating the acid with an excess of phosphorus pentachloride and pouring the mixture over ice. It is very easily soluble in ether and very sparingly soluble in petroleum. It separates from ether–light petroleum in colourless, compact crystals, m. p. 98—102° (Found : Cl, 56·5. $C_{11}H_5O_3Cl_7$ requires Cl, 57·3%).

The *amide*, obtained by gently heating the acid chloride with a mixture of equal parts of strong ammonia solution and alcohol, was easily soluble in boiling alcohol, from which it separated in long, colourless prisms, m. p. 195·5—197° (Found : Cl, 51·2; N, 3·2. $C_{11}H_7O_3NCl_6$ requires Cl, 51·4; N, 3·4%).

Action of Alcoholic Potassium Hydroxide upon Anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene. — *Isolation of 5-carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene* (III). 20 G. of the acid (1 mol.) were added gradually to a hot solution of 48 g. of potassium hydroxide (18 mols.) in 200 c.c. of alcohol, and the mixture was gently boiled for ½ hour. Boiling water (200 c.c.) was added, and the alcohol distilled in steam. The dark red solution thus obtained deposited, on cooling, the potassium salt of 5-carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene in colourless, thin, flaky plates. These were filtered off and treated with dilute hydrochloric acid. The *acid*, isolated by means of ether and obtained as a crystalline, colourless mass, separated from warm ether–light petroleum in small, compact crystals (yield, 8·1 g.), m. p. 124—126° (Found : C, 41·9; H, 3·5; Cl, 33·8. $C_{11}H_{11}O_4Cl_3$ requires C, 42·15; H, 3·6; Cl, 33·9%).

It is very sparingly soluble in water or petroleum and easily soluble in ether or alcohol. It forms with alkalis colourless salts which are sparingly soluble in water.

Identification of 2-hydroxy-1 : 5-isophthalic acid (V). The dark red mother-liquor from the preceding potassium salt was acidified with hydrochloric acid. The acid set free, which in part crystallised, was extracted with ether. Partial evaporation of the ether and addition of a little light petroleum gave 3·2 g. of a microcrystalline product, consisting mainly of 2-hydroxy-1 : 5-*iso*phthalic acid. As it was difficult to separate this acid in a pure condition, it was

identified by conversion into its *ethyl* ester. This, after two crystallisations from methyl alcohol, melted sharply at 52·5° (Found: C, 60·2; H, 6·1. $C_{12}H_{14}O_5$ requires C, 60·4; H, 5·9%).

Identification of 5-carboxy-2-ethoxyphenylglycollic acid (IV). On allowing the ethereal mother-liquor from which the 2-hydroxy-1 : 5-*iso*phthalic acid had separated to evaporate spontaneously, an acid crystallised in colourless, silky needles, but in too small quantity to admit of complete purification. It was shown to be mainly 5-carboxy-2-ethoxyphenylglycollic acid in the following way. A solution of the acid (1·6 g.) in 3 c.c. of concentrated sulphuric acid was heated on a water-bath for 10 minutes, cooled, and poured into water. The product, isolated by means of ether, was a brown, crystalline solid which sublimed in colourless needles; these softened at 235°, melted at 244°, and agreed in properties with 5-carboxy-2-hydroxybenzaldehyde (Tiemann and Reimer, *Ber.*, 1876, 9, 1274). It dissolved easily in hot water, and the solution gave a yellow colour with sodium hydroxide and a dark red colour with ferric chloride. It reacted with semicarbazide, yielding a well-crystallised semicarbazone.

The *phenylhydrazone*, which separated as a yellow solid when phenylhydrazine was added to a hot aqueous solution of the aldehyde, crystallised from boiling alcohol, in which it was moderately easily soluble, in yellow needles, m. p. 257—258° (decomp.) (Found: N, 10·2. $C_{14}H_{12}O_3N_2$ requires N, 10·9%).

An alcoholic solution of the hydrazone is acid to litmus and gives a strong orange coloration with ferric chloride.

Oxidation of 5-Carboxy-2-ethoxyphenylglycollic Acid (IV) *to 2-Hydroxy-1 : 5-isophthalic Acid* (V) *by Alkaline Potassium Permanganate.*—When the aqueous alkaline solution of the products of the action of potassium ethoxide upon anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene, obtained by diluting the mixture and distilling off the alcohol, was boiled and treated with a dilute aqueous solution of potassium permanganate until the colour of this was no longer discharged, a yellow solution was obtained. This was filtered from manganese dioxide, concentrated, and acidified with sulphuric acid. Ether then extracted 2-hydroxy-1 : 5-*iso*phthalic acid, from which the well-characterised ethyl ester was prepared.

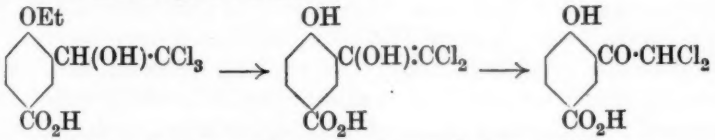
The action of alcoholic potash upon the condensation product of *p*-hydroxybenzoic acid and chloral therefore takes place in the three stages (III ⟶ IV ⟶ V) shown on p. 687.

The action of alcoholic potash upon anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene is much less violent than its action upon the analogously

constituted 5-nitro-compound, owing to the greater stability of the first product, 5-carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene, which reacts with alcoholic potash sufficiently slowly to admit of its isolation as above described.

Action of Sulphuric Acid upon 5-Carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (III) *and Formation of ωω-Dichloro-5-carboxy-2-hydroxyacetophenone* (VI).—A mixture of 10 g. of 5-carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene and 100 c.c. of concentrated sulphuric acid was heated for 10 minutes on a water-bath; hydrogen chloride was then liberated. After cooling, the dark brown solution was poured into 500 c.c. of water, and the product, *ωω-dichloro-5-carboxy-2-hydroxyacetophenone*, which was mainly deposited as a colourless solid, was extracted with ether. On evaporation of the ether, a well-crystallised product was left which was moderately easily soluble in water and easily soluble in alcohol. It separated from a mixture of these solvents in thin, unctuous plates, m. p. 163—166°. When powdered, it is extremely irritating and causes violent sneezing (Found: C, 43·4; H, 2·7; Cl, 28·45. $C_9H_6O_4Cl_2$ requires C, 43·4; H, 2·4; Cl, 28·5%).

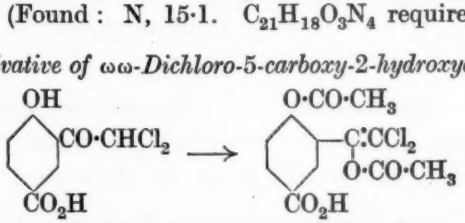
The compound must be formed by the elimination of hydrogen chloride under the influence of sulphuric acid followed by an intramolecular rearrangement thus:



ωω-Dichloro-5-carboxy-2-hydroxyacetophenone yields an *osazone* and a well-crystallised semicarbazone.

The osazone was obtained by gently boiling a slight excess of phenylhydrazine with a fairly concentrated alcoholic solution of the acetophenone. It separated as a yellow, crystalline mass and was recrystallised from boiling alcohol, in which it was moderately easily soluble, and from which it separated in canary-yellow needles, m. p. 243·5° (Found: N, 15·1. $C_{21}H_{18}O_3N_4$ requires N, 15·0%).

Acetyl Derivative of ωω-Dichloro-5-carboxy-2-hydroxyacetophenone.



—2 G. of the dichloro-acetophenone and 1 g. of anhydrous sodium acetate were added to 20 c.c. of acetic anhydride and heated gradually on an oil-bath. The liquid was allowed to boil gently for a few

seconds, cooled, and poured into water; the viscid mass thus obtained was recrystallised from alcohol, from which it separated in colourless needles, m. p. 194—196° (Found: Cl, 21·5; C, 46·5; H, 3·1. $C_{13}H_{10}O_6Cl_2$ requires Cl, 21·3; C, 46·8; H, 3·0%).

Preparation of 5-Carboxy-2-hydroxyacetophenone, by Reduction of ωω-Dichloro-5-carboxy-2-hydroxyacetophenone (VI).—2 G. of ωω-dichloro-5-carboxy-2-hydroxyacetophenone and 25 c.c. of hydriodic acid (b. p. 126°) were heated to 115—120° for a short time. Reduction occurred very easily, free iodine was liberated, and on cooling the liquid *5-carboxy-2-hydroxyacetophenone* crystallised out. It was recrystallised from dilute alcohol, from which it separates in colourless, shining plates, m. p. 246—247° (Found: C, 59·9; H, 4·4. $C_9H_8O_4$ requires C, 60·0; H, 4·4%).

It is sparingly soluble in water and easily soluble in alcohol. Its aqueous solution gives a cherry-red coloration with ferric chloride.

It yields a well-characterised *phenylhydrazone* when its concentrated alcoholic solution is heated with a slight excess of phenylhydrazine. This is sparingly soluble in alcohol, from which it separates in long, pale-yellow needles, m. p. 286° (Found: N, 10·2. $C_{15}H_{14}O_3N_2$ requires N, 10·4%).

The Action of Hydriodic Acid on 5-Carboxy-2-ethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (III).—2·7 G. of the substance were boiled gently for a short time with 25 c.c. of hydriodic acid (b. p. 126°). Iodine was liberated and, on cooling, 5-carboxy-2-hydroxyacetophenone crystallised out. After being recrystallised from dilute alcohol, it was obtained in shining plates, identical with those obtained by reduction of ωω-dichloro-5-carboxy-2-hydroxyacetophenone, and giving the same phenylhydrazone with phenylhydrazine.

In conclusion we desire to thank the "Real Academia de Ciencias" of Madrid and the Ramsay Memorial Fellowship Trust for the Fellowship awarded to one of us (F. C. P.) which enabled this work to be carried out.

THE QUEEN'S COLLEGE, OXFORD. [*Received, December 23rd*, 1926.]

CIV.—*The Mechanism of Reactions induced by Hydrogen Chloride between Aromatic Aldehydes and Aldehydecyanohydrins in Solution.*

By BERTRAM HOBART INGHAM.

THE object of this research was to elucidate the mechanism of the formation of oxazoles and other substances by the action of hydrogen

chloride upon ethereal solutions of aromatic aldehydes and aldehydecyanohydrins. Fischer (*Ber.*, 1896, **29**, 205) first employed this method to prepare 2 : 5-diphenyloxazole, the constitution of which he established by an alternative synthesis and by degradation, but he made no suggestion as to the mode of formation of the final products.

The action of hydrogen chloride upon ethereal solutions (both dry and moist) of aldehydecyanohydrins, alone and also in the presence of aldehydes, has now been investigated, and, besides oxazoles, mandelamide derivatives and 3-keto-2 : 5-diaryl-3 : 4-dihydro-1 : 4-diazines have been obtained. The example studied in greatest detail was that of benzaldehyde and benzaldehydecyanohydrin (mandelonitrile), and the most salient observations made in connexion with this aldehyde and its derivatives may be summarised as follows :

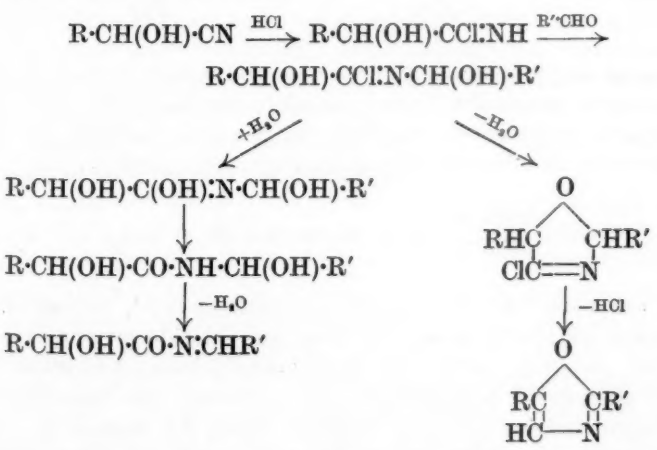
(1) Exclusion of moisture favoured oxazole formation and inhibited the production of mandeloarylideneamides, and *vice versa*.

(2) The " blocking " of the hydroxyl group of the cyanohydrin (*e.g.*, by benzoylation or by substitution of chlorine) precluded oxazole formation.

(3) Iminochlorides were produced as intermediates.

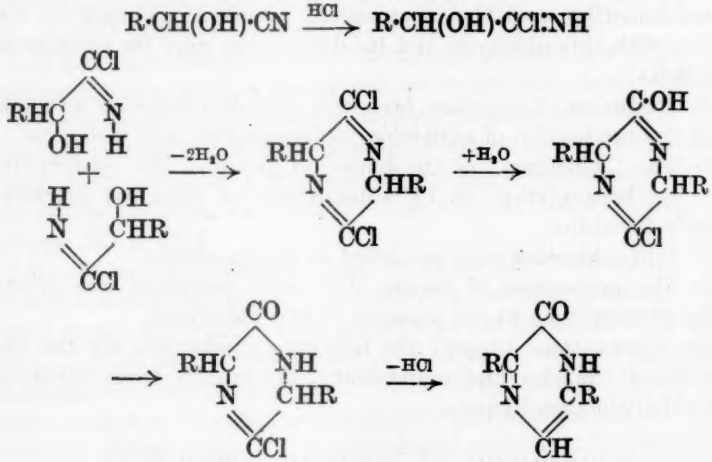
(4) The proportion of diazine derivative produced was greater in the absence than in the presence of free aldehyde.

The observations support the following mechanism for the production of oxazoles and mandeloarylideneamides from aldehydes and aldehydecyanohydrins :

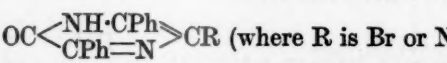


The diazine obtainable from benzaldehydecyanohydrin was first prepared from that substance by Minovici (*Ber.*, 1899, **32**,

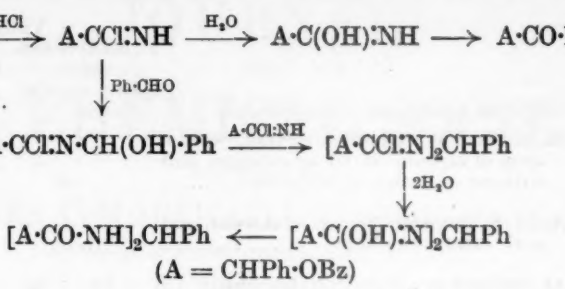
2206), who, however, assigned to it an extremely improbable structure. Later, Japp and Knox (J., 1905, **87**, 701) determined its constitution, but not its mode of formation. In this connexion, the generalisations (3) and (4) given above, and the statement of Japp and Knox (*loc. cit.*) that " . . . attempts to obtain the condensation product by acting on mandelonitrile with other dehydrating agents did not give the desired result . . ." are highly significant; they seem, however, to have been overlooked by previous workers. These observations support the following mechanism for the production of 3-keto-2 : 5-diaryl-3 : 4-dihydro-1 : 4-diazines from aromatic aldehydecyanohydrins :



Minovici also prepared a monobromo- and a mononitro-derivative of the diazine obtainable from benzaldehydecyanohydrin, and their formation is quite consistent with the structure assigned by Japp and Knox to this diazine if they are formulated thus :



The condensation of benzoylmandelonitrile with benzaldehyde in ethereal solution in presence of hydrogen chloride gave no oxazole, but two isomeric forms of benzylidenebisbenzoylmandelamide. In the absence of benzaldehyde and moisture, the iminochloride of benzoylmandelonitrile was obtained, whilst if a trace of moisture was present benzoylmandelamide was produced. For similar reasons to those given for the production of oxazoles, the mechanism of the reactions would appear to be as follows :



EXPERIMENTAL.

General.—Hydrogen cyanide was prepared by Wade and Panting's method (J., 1898, **73**, 255), and redistilled over phosphorus pentoxide (except in experiments 1 and 2 of the benzaldehydecyanohydrin series). It was condensed with the aldehyde by being kept for at least 20 hours with this in ethereal (or ether–benzene) solution in the presence (except in the experiments 1 and 2 mentioned above) of tripropylamine as a basic catalyst (Ultée, *Rec. trav. chim.*, 1909, **28**, 718). The solvents required were dried with sodium and redistilled over phosphorus pentoxide, and the hydrogen chloride was dried with sulphuric acid and calcium chloride. The liquid aldehydes were redistilled several times in a vacuum, and the solid aldehydes (B.D.H.) were dried in a vacuum over concentrated sulphuric acid.

Condensation of Benzaldehydecyanohydrin and Benzaldehyde (compare Fischer, *loc. cit.*).—In each experiment benzaldehydecyanohydrin (12·5 g.; 1 mol.) and benzaldehyde (10 g.; 1 mol.) in 60 c.c. of dry ether were employed. After cyanohydrin formation had taken place (as described above), the solution, protected from moisture, was saturated at 0° with hydrogen chloride. The oxazole and mandelamide thus produced were separated by fractional crystallisation from alcohol and ligroin.

An ethereal solution of α-chlorophenylacetonitrile (see below) was saturated with hydrogen chloride, 1 mol. of benzaldehyde then added, and the passage of hydrogen chloride continued. An unidentified substance was obtained, but no 2 : 5-diphenyloxazole or mandelobenzylideneamide was detected in the product.

α-Chlorophenylacetonitrile was prepared by the action of thionyl chloride upon benzaldehydecyanohydrin in ethereal solution and obtained as a greenish-yellow, pungent liquid, b. p. 170°/ about 120 mm. It has an irritant action on the skin, and its vapour is a strong lachrymatory (compare Michaël and Jeanprêtre, *Ber.*, 1892, **25**, 1679).

Expt.	Special conditions of experiment.	Yields. 2 : 5-Diphenyloxazole hydrochloride. Grams.	%	Mandelobenzylideneamide. Grams.	%
1	As in (3), but without a solvent, with a drop of aqueous KOH as catalyst, and without exclusion of moisture.....	nil		nearly theoretical	
2	As in (3), but with 200 c.c. of solvent, and with catalyst as in (1)	trace		nearly theoretical.	
3	As outlined in the general description ...	14	58	7	31
4	As in (3); the cyanohydrin, however, was frozen in solid CO_2, and the highest-melting fraction (m. p. about 15°) employed *	10·5	43	8	36
5	As in (3), with addition of 7 g. of anhydrous zinc chloride	nil	—	15	67
6	As in (3), with addition of 15 g. of thionyl chloride immediately before passage of hydrogen chloride	9	37	nil ‡	—
7	As in (6), but with more rapid passage of hydrogen chloride.†	14	58	nil ‡	—

* Ultée (*loc. cit.*) gives the m. p. of pure benzaldehydecyanohydrin as 21·5—22°.

The relatively larger proportion of mandelobenzylideneamide obtained in this than in the previous experiment is explained by the assumption that the cyanohydrin absorbed a little atmospheric moisture during the process of freezing.

† The larger yield of oxazole hydrochloride in this case than in the previous one is in accordance with theoretical considerations—the condensation taking place more rapidly, the thionyl chloride would have less time in which to "block" the hydroxyl group of the cyanohydrin and thus prevent oxazole formation.

‡ A considerable quantity of α-chlorophenylacetonitrile was formed in each case.

Condensation of Benzoylmandelonitrile and Benzaldehyde.—By the action of hydrogen chloride upon an ethereal solution of benzoylmandelonitrile (Francis and Davis, J., 1909, **95**, 1403) and benzaldehyde in molecular proportion, a white solid was produced, which was separated into two portions by extraction with alcohol for several hours. The residue, which was insoluble in acetone, acetic acid, and benzene, melted at 250—251° (Found: C, 74·0; H, 5·3; N, 5·1. $C_{37}H_{30}O_6N_2$ requires C, 74·2; H, 5·0; N, 4·7%); the sparingly soluble portion was an isomeride and crystallised from alcohol in microscopic needles, m. p. 223—224° (Found: C, 74·2; H, 5·5; N, 5·1%). 2 : 5-Diphenyloxazole could not be detected in the original alcoholic mother-liquor, even after concentration, by means of picric acid.

The two isomerides were readily debenzoylated by alcoholic